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REMARKS

The Office Action discusses the examination of claims 1-20. This amendment cancels claim 14 and changes the text of claims 1-13, 15-17, 19 and 20. New claims 21 and 22 have been added. The amendments to the claims address the rejections made under 35 USC 112. New claim 21 is supported by original claim 20. New claim 22 is supported by original claim 14.

Support for "alkaline earth metal salt" in claim 1 can be found at page 11, line 23 of the specification. The amendment at page 8, line 16 is supported by page 8, line 20. The amendment at page 15, line 10 is supported by the examples at page 15, lines 10-16. The amendment at page 15, line 11 is supported by the English translation of the priority document, and "Chemical Handbook, 3rd revised edition, Chapter II (edited by Japanese Chemical, published by Maruzen; Japan), attached. The amendment at page 21, line 2 is supported by page 21, line 22. The amendment at page 27, line 3 is supported by page 19, lines 6-9 of the specification.

The English translation of the Priority Document 66501/1998 supports the amendments to the specification at pages 19, 30, 34, 36 and 37. No new matter has been added by these amendments.

Claim Rejection under 35 USC §112

Claims 1-20 have been rejected under 35 USC § 112, second paragraph, as claiming indefinite subject matter.

Regarding claim 1, the rejection points out that, in claim 1, it is indefinite whether a compound or a composition was being claimed, and the terms "acidic form" and "effective amount" were not clear. Claim 1 has been amended based on page 6, lines 4 to 14 and page 11, lines 16 to 19 of the specification. Claim 1 now recites that the cellulose acetate of the present invention is obtained by the reaction of a cellulose, which may contain a hemicellulose, with acetic anhydride in the presence of sulfuric acid catalyst. Claim 1 also recites that feature (i) is directed to the cellulose acetate having carboxyl groups wherein at least part of the carboxyl groups are free carboxyl groups. Additionally, in feature (iii) of claim 1, the phrase "from effective amount to 5.5×10^{-6} equivalent" has been revised to recite " 5.5×10^{-6} equivalent or less" based on page 19, line 9 of the specification.

Regarding claim 5, the rejection states that the phrase "derivative thereof" is not clear. That phrase has been canceled from the claims.

Regarding claims 11 and 12, the rejection states that the term "slurry pH" is indefinite. The slurry pH is described at page 25, line 2 to page 26, line 2 of the specification and refers to the pH of the slurry when the cellulose acetate is in the form of a slurry. Accordingly, in claims 11 and 12 the phrase "which has the slurry pH of..." has been amended to recite "wherein the cellulose acetate is in the form of a slurry, and wherein the slurry has a pH of..." which incorporates the description from the specification.

Regarding claim 14, the rejection is directed to the use of "and/or" which allegedly renders the claim indefinite. Claim 14 has been canceled and replaced with new claim 22 which is supported at page 6, line 4 to page 7, line 16 of the specification.

Regarding claim 20, the rejection was based on the absence of process steps for carrying out the invention. Claim 20 has been rewritten as independent claims 20 and 21 which clearly recite the process steps.

Claim Rejection Under 35 USC § 103

Claims 1-19 have been rejected under 35 USC § 103(a) as being obvious over Ishii et al. (US 3,816,150). Claims 18-20 have been

rejected under 35 USC § 103(a) as being obvious over Seo et al. (US 5,240,665) in view of Ishii et al. This rejection is respectfully traversed. Reconsideration and withdrawal thereof are requested.

The Present Invention

The cellulose acetate of the present invention is obtained by the reaction of a cellulose, which may contain a hemicellulose, with acetic anhydride in the presence of a sulfuric acid catalyst. The cellulose acetate further has at least one feature selected from the group consisting of (i), (ii) and (iii) as described in claim 1.

Distinction from Ishii et al.

Ishii et al. discloses a process for making modified cellulose acetate which comprises forming or molding mixed cellulose ester made by esterifying (a) cellulose with (b) acetic acid and (c) polybasic carboxylic acid, and treating the formed or molded product with a liquid treating agent consisting essentially of an aqueous solution of a water-soluble polyvalent metal salt.

In contrast, a cellulose acetate of the present invention is obtained by the reaction of a cellulose with acetic anhydride in

the presence of sulfuric acid catalyst without a polybasic carboxylic acid. Therefore, the cellulose acetate of Ishii et al. is quite different from that of the present invention. Ishii et al. can be further distinguished as follows:

Regarding feature (i), the rejection argues that the modified cellulose acetate of Ishii et al. has a free carboxyl group, and thus is within the scope of feature (i) of claim 1. However, the free carboxyl group of the mixed cellulose ester of Ishii et al. is derived from a polybasic carboxylic acid residue generated by the esterification of a cellulose with polybasic carboxylic acid. In comparison, the free carboxyl group of the cellulose acetate of the present invention is derived from a cellulose which may contain a hemicellulose as a raw material.

The instant Examples describe a cellulose triacetate, which does not require a hydroxyl group as a reaction site for the esterification with polybasic carboxylic acid. In Ishii et al., the esterification of a cellulose with polybasic carboxylic acid requires a hydroxyl group as a reaction site. Thus, it is predicted that a cellulose triacetate, which does not require a hydroxyl group, is not suggested by Ishii et al.

In support of the above argument, attached are two references: (L1) "SEN-I GAKKAISHI, vol.48, No. 11(1992)" and (L2)

"MOKUZAI-KAGAKU (Wood Chemistry), page 319, edited by N. Migita, Y. Yonezawa, and T. Kondo, published by Kyoritu; Japan, 1974)". The L1 reference describes that the content of a carboxyl group in cellulose and pulp samples was measured according to TAPPI Test Methods (page 650, right column, lines 6-7). It shows a relationship between the carboxyl content of the original sample (microcrystalline cellulose powder, linter cellulose, softwood bleached kraft pulp, hardwood bleached kraft pulp) and the ξ potential of a corresponding amorphous particles in distilled water (see page 652, Fig. 5 and the sixth line to the first from the bottom of the right column, page 652). The reference L2 describes that "in a process for producing a pulp, when hydrolysis or oxidation acts on a chain or linear molecule (of a cellulose and a hemicellulose), the increase of a reductive end group by scission of the chain molecule, or the oxidation of a hydroxyl group in the chain molecule generates a carbonyl group or a carboxyl group." See page 319, lines 1-3. Thus, references L1 and L2 demonstrate that a pulp (cellulose) has a carboxyl group.

Regarding feature (ii), Ishii et al. describes maleic acid, succinic acid, etc. as polybasic carboxylic acids for the esterification of cellulose. See the first column, lines 47-48. However, Ishii et al. fails to disclose or suggest that an acid

has the specific pKa (1.93-4.50) as recited in instant claim 1. Ishii et al. can be further distinguished in this regard in that the specific acid and metal salts thereof in the present invention are not used for the esterification of a cellulose.

Furthermore, in the present invention, the acid having the specific pKa or its metal salt is used to generate the free carboxyl groups. See page 20, lines 22-25. The metal salt of the acid is used to retain or itself becomes the free carboxyl groups, and is effective in improving the heat resistance. However, in Ishii et al., there is no suggestion that the specific acid and metal salts thereof play this role. In Ishii et al., a polybasic carboxylic acid is used for the esterification with cellulose. Therefore, the role or function of the acid in the present invention is quite different from that of Ishii et al.

Regarding feature (iii), Ishii et al. describes that the mixed ester of cellulose is treated with a divalent or higher metal salt to increase the solvent resistance. See column 2, lines 37-41. Thus, the carboxyl groups are utilized for crosslinking with the polyvalent metal. Ishii et al. fails to disclose or suggest the importance of the total content of the alkali metal and the alkaline earth metal in 1 gram of the cellulose acetate. In the present invention, the total content of

the alkali metal and the alkaline earth metal affect the generation of a free carboxyl group and improve heat resistance (page 19, lines 5-23). Further, when the total content of the alkali metal and the alkaline earth metal in 1 gram of the cellulose acetate is 5.5×10^{-6} equivalent or less, the releasing (peeling) resistance of a semi-dried film containing the above cellulose acetate can be reduced (page 19, lines 20-23). Thus, the role or function of the metal in the present invention differs significantly from that of Ishii et al.

Inasmuch as Ishii et al. does not make the presently claimed invention *prima facie* obvious for the reasons stated above, the rejection of claims 1-19 under 35 U.S.C. § 103 over these cited references should be withdrawn.

Additional evidence of non-obviousness

The present invention is further characterized by exhibiting the following unexpected advantages over the prior art. The cellulose acetate, when obtained by the reaction of a cellulose with acetic anhydride in the presence of sulfuric acid catalyst and having at least one feature selected from (i), (ii) and (iii) according to the present invention, has a remarkable effect on the releasability and transparency of a film, and on the spinnability

of a dope containing the cellulose acetate as evidenced by the instant Examples.

Further, as mentioned above, the releasability, transparency and spinnability properties can be improved even when a cellulose triacetate, which can not be used for the esterification with polybasic carboxylic acid, is employed. Moreover, in Ishii et al., the solvent resistance is increased by treating the mixed cellulose ester with a divalent or higher metal salt. Consequently, the mixed cellulose ester of Ishii et al. cannot be soluble in a solvent, that is, a dope cannot be formed. This is evidenced by observing the comparison between Example 4 of the present invention and the Examples of Ishii et al. at column 3, Example 1 and Table 1. This is an unexpected advantage which is sufficient to demonstrate the unobviousness of the present invention over Ishii et al. Accordingly, the skilled artisan would not be motivated by the teachings of Ishii et al. to use the instant process for obtaining the cellulose acetate with the expectation of obtaining a product exhibiting the improved effects as are seen in the present invention (i.e., the improvement of the releaseability of the film obtained by casting a dope and the improvement of the spinnability of a dope).

Accordingly, a *prima facie* case of obviousness has not been established with respect to Ishii et al. and the rejection under 35 USC 103 over Ishii et al. should be withdrawn.

Distinction from Seo et al.

Seo et al. discloses a process for the production of cellulose acetate fibers which comprises mixing cellulose acetate, acetone, a metal oxide precursor, acid and water, filtering and spinning the solution.

Seo et al. is cited to teach the use of a dope containing a cellulose acetate. Seo et al. fails to teach the cellulose acetate bound by carboxyl groups in acidic form. The rejection relies on Ishii et al. to correct the deficiencies of Seo et al. However, as discussed above, Ishii et al. teaches the skilled artisan to increase the solvent resistance by treating the mixed cellulose ester with a divalent or higher metal salt. As a result, the mixed cellulose ester of Ishii et al. will not be soluble in a solvent. Therefore, a dope cannot be formed.

Thus, the skilled artisan in possession of both Seo et al. and Ishii et al., would not have an expectation of success in using the cellulose acetate of Ishii et al. in a dope according to Seo et al. Absent the requisite motivation in either Seo et al.

or Ishii et al. to alter Ishii et al. so as to arrive at a cellulose acetate suitable for a dope, it cannot be said that a *prima facie* case of obviousness has been established by the combination of these two references.

Inasmuch as Seo et al. does not make the presently claimed invention *prima facie* obvious, and the defects are not cured by the combination with Ishii et al., the rejection of claims 18-20 under 35 U.S.C. § 103 over these cited references should be withdrawn.

The present application describes a novel, useful invention. The above amendments and remarks provide for an enabling description of the invention and claims to patentable subject matter. Thus, Applicants respectfully request allowance of claims 1-13 and 15-22.


Pursuant to 37 CFR 1.17 and 1.136(a), the Applicants respectfully petition for a one (1) month extension of time for filing a response in connection with the present application and the required fee of \$110.00 is attached hereto.

Serial No. 09/145,987

If necessary, the Commissioner is hereby authorized in this, concurrent, and further replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fee required under 37 C.F.R. 1.16 or under 37 C.F.R. 1.17; particularly, extension of time fees.

Respectfully yours,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

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RCS/~~LSL~~/afy

Attachments: Reference: SEN-I GAKKAISHI, vol.48, No. 11(1992)
 Reference: MOKUZAI-KAGAKU (Wood Chemistry), page
 319, edited by N. Migita, Y. Yonezawa, and
 T. Kondo, published by Kyoritu;
 Japan, 1974)".
 Reference: Chemical Handbook, 3rd revised edition,
 Chapter II (edited by Japanese Chemical,
 published by Maruzen; Japan
 English Translation of JP 66501/1998

10・2・3 水溶液中の有機化合物の解離定数

10・2・3 dissociation constant of organic compounds in aqueous solution

compound dissociation stage

表 10・11 有機化合物の酸解離指数¹⁾ (1) → Table 10・11 acid dissociation index of organic compounds (1)

化合物	解離段階	pK _a	t/°C	イオン強度	化合物	解離段階	pK _a	t/°C	イオン強度
アクリル酸		4.26	25	0	L-アラニルグリシン	1	3.10	25	0.1
アジピン酸	1	4.26	25	0.1		2	8.09	25	0.1
	2	5.03	25	0.1	β-アラニルグリシン	1	3.18	25	0.1
L-アスコルビン酸	1	4.03	25	0.1		2	9.41	25	0.1
	2	11.34	25	0.1	β-アラニル-L-ヒスチジン (L-カル	2	6.75	25	0.1
アスパラギン	1	2.14	25	0.1	ニン)	3	9.32	25	0.1
	2	8.72	25	0.1	アラニン	1	2.30	25	0.1
アスパラギン酸	1	1.93	25	0.1		2	9.69	25	0.1
	2	3.70	25	0.1	β-アラニン	1	3.53	25	0.1
	3	9.63	25	0.1		2	10.10	25	0.1
アセチルアセトン		8.80	25	0.1	β-アラニンアミド		9.19	25	0.1
N-アセチルアラニン		3.72	25	0	アルギニン	1	2.05	25	0.1
N-アセチルグリシン		3.47	25	0.1		2	9.01	25	0.1
アゼライン酸	1	4.39	25	0.1	安息香酸		4.20	25	0
	2	5.12	25	0.1	イソ吉草酸		4.68	25	0.1
アデニン	2	4.07	25	0.1	イソキノリン		5.38	20	0
	3	9.67	25	0.1	イソニコチンアミド		3.68	25	1.0
アデノシン	1	4.50	25	0	イソニコチン酸	1	1.79	25	0
	2	12.35	25	0		2	4.87	25	0
5'-アデノシン三リン酸	4	4.06	25	0.1	イソニコチン酸メチル		3.26	22	0
	5	6.51	25	0.1	イソ酪酸		4.63	25	0.1
2'-アデノシンリン酸	2	3.72	25	0.1	イソロイシン	1	2.32	25	0
	3	6.02	25	0.1		2	9.75	25	0
3'-アデノシンリン酸	2	3.65	25	0.1	イソシリン酸	1	1.5	20	0
	3	5.83	25	0.1		2	8.96	25	0
5'-アデノシンリン酸	2	3.80	25	0.1		3	12.36	25	0
	3	6.19	25	0.1	5'-イノシンリン酸	2	6.64	25	0
o-アニス酸		4.09	25	0	イミダゾール	1	6.99	25	0
m-アニス酸		4.09	25	0		2	14.44	25	0
p-アニス酸		4.48	25	0	ウラシル		9.49	25	0
アニリン		4.65	25	0.1	エタンチオール		10.61	25	0
m-アニリンスルホン酸(メタニル酸)		3.74	25	0	エチルアミン		10.63	25	0
p-アニリンスルホン酸(スルファニル酸)		3.23	25	0	エチレンジアミン	1	7.08	25	0.1
o-アミノ安息香酸(アントラニル酸)	1	2.02	25	0		2	9.89	25	0.1
	2	4.95	25	0	オイゲノール		10.17	25	0
m-アミノ安息香酸	1	3.12	25	0	オキサロ酢酸	1	2.27	25	0.1
	2	4.74	25	0		2	3.89	25	0.1
p-アミノ安息香酸	1	2.41	25	0	オクタン酸		4.89	25	0
	2	4.85	25	0	オルニチン	1	1.71	25	0
2-アミノエタノール		9.52	25	0.1		2	8.74	25	0.1
2-アミノエタンチオール(システ	1	8.21	25	0.1		3	10.55	25	0.1
アミン)	2	10.71	25	0.1	カテコール	1	9.23	25	0.1
5-(2-アミノエチル)-1H-イミダ	1	6.07	25	0.1		2	13.0	25	0.1
ゾール(ヒスタミン)	2	9.83	25	0.1	ギ酸		3.55	25	0.1
2-アミノピリジン	2	6.70	25	0.2	キサントシン	1	7.53	25	0
3-アミノピリジン	2	6.06	25	0.1		2	11.84	25	0
4-アミノピリジン	2	9.14	25	0.2	キサントシン	2	5.67	25	0
o-アミノフェノール	1	4.74	25	0.1		3	12.00	25	0
	2	9.87	25	0.1	吉草酸		4.64	25	0.1
4-アミノ酪酸	1	4.03	25	0	ギザルジシ酸	2	4.75	25	0.1
	2	10.56	25	0	8-キノリノール	1	4.99	25	0.1
L-アラニル-L-アラニン	1	3.20	25	0.1		2	9.66	25	0.1
L-アラニルグリシルグリシン	1	3.18	25	0.16	キノリン		4.97	25	0.1
	2	7.85	25	0.16	グアニジン		13.54	27	1.0
L-アラニルグリシルグリシン	1	3.24	25	0.16		1	3.3	25	0.1
	2	7.93	25	0.16		2	9.31	25	0.1
β-アラニルグリシルグリシン	1	3.19	25	0.1		3	12.3	25	0
	2	9.25	25	0.1	グアニン	1	1.8	25	0.1
						2	9.13	25	0.1

1) 本表の数値は主として A. E. Martell, R. M. Smith, "Critical Stability Constants", Vol. 1~3, Plenum Press (1974, 1975, 1977) から引用した。

イオン強度 0.5 mol dm⁻³
(ClO₄), 20°C

イオン強度 0.5 mol dm⁻³
(ClO₄), 20°C

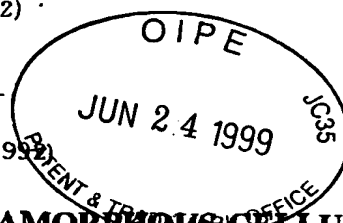
with, A. E. Martell,
Complexes", Part

compound dissociation stage 表 10-11 有機化合物の酸解離指数 (2) → Table 10-11 acid dissociation index of organic compound (2)

化合物	解離段	pK _a	t °C	イオン 強度	化合物	解離段	pK _a	t °C	イオン 強度
クエン酸	1	2.87	25	0.1	ケイ皮酸 (cis-)		3.88	25	0
	2	4.35	25	0.1	ケイ皮酸 (trans-)		4.44	25	0
	3	5.69	25	0.1	コハク酸	1	4.00	25	0.1
グリオキシル酸		3.18	20	0.1		2	5.24	25	0.1
グリコール酸		3.63	25	0.1	酢 酸		4.56	25	0.1
グリシル-L-アラニン	1	3.07	25	0.1	サリチルアルデヒド		8.13	25	0.1
	2	8.12	25	0.1	サリチル酸 (o-ヒドロキシ安息香酸)	1	2.81	25	0.1
グリシル-β-アラニン	1	3.91	25	0.1		2	13.4	25	0.1
	2	8.09	25	0.1	サルコシン	1	2.20	25	0.1
グリシルグリシル-L-アラニン	1	3.18	25	0.16		2	9.99	25	0.1
	2	7.90	25	0.16	m-シアノ安息香酸		3.60	25	0
グリシルグリシルグリシルグリシン	1	3.18	25	0.1	p-シアノ安息香酸		3.55	25	0
	2	7.87	25	0.1	シアノ酢酸		2.47	25	0
グリシルグリシルグリシル-L-ヒスチジン	1	2.90	25	0.16	o-シアノフェノール		6.86	25	0.1
	2	6.73	25	0.16	ジェタノールアミン		8.90	25	0.1
	3	7.99	25	0.16	ジエチルアミン		10.93	25	0
グリシルグリシルグリシン	1	3.20	25	0.1	5,5-ジエチルバルビツル酸 (バルビタル)		7.78	25	0.1
	2	7.89	25	0.1	ジエチレントリアミン	1	4.23	25	0.1
グリシルグリシル-L-ヒスチジン	1	2.72	25	0.16		2	9.02	25	0.1
	2	6.75	25	0.16		3	9.84	25	0.1
	3	8.10	25	0.16	シクロヘキサンカルボン酸		4.70	25	0.1
グリシルグリシル-L-ロイシン	2	7.90	25	0.1	シクロヘキシルアミン		10.64	25	0
グリシル-DL-ヒスチジルグリシン	1	3.26	25	1.0	ジクロロ酢酸		1.30	25	0
	2	6.92	25	1.0	シスチン	3	8.03	20	0.15
	3	7.96	25	1.0		4	8.80	20	0.15
グシリン-L-ヒスチジン	1	2.54	25	0.16	システイン	1	1.88	25	0.1
	2	6.68	25	0.16		2	8.15	25	0.1
	3	8.09	25	0.16		3	10.29	25	0.1
グリシル-L-ロイシン	1	3.09	25	0.1	シチジン	1	4.08	25	0
	2	8.14	25	0.1		2	12.5	25	0
グリシン	1	2.36	25	0.1	シトシン	1	4.58	25	0
	2	9.57	25	0.1		2	12.15	25	0
グリシンアミド		7.93	25	0.1	シトルリン	1	2.43	25	0.1
2-グリセリンリン酸	1	1.34	25	0		2	9.41	25	0.1
	2	6.65	25	0	3,4-ジヒドロキシフェニルアラニン (DOPA)	1	2.31	25	1.0
D-グルコース 1-リン酸	1	1.46	25	0.1		2	8.65	25	0.1
	2	6.50	25	0		3	9.78	25	0.1
γ-L-グルタミル-L-システイニルグリシン (還元型グルタチオン)	1	2.03	37	0.15		4	13.40	25	1.0
	2	3.44	37	0.15	ジベンゾイルメタン		13.75	30	0
	3	8.38	37	0.15	ジメチルアミン		10.77	25	0
	4	9.29	37	0.15	N,N'-ジメチルエチレンジアミン	1	7.01	25	0.1
グルタミン	1	2.17	25	0.1		2	9.98	25	0.1
	2	9.01	25	0.1	2,3-ジメルカプトプロパノール (BAL)	1	8.58	25	0.1
グルタミン酸	1	2.18	25	0.1		2	10.68	25	0.1
	2	4.20	25	0.1	N,N'-ジメチルグリシン	1	2.08	25	0.1
	3	9.59	25	0.1		2	9.80	25	0.1
グルタル酸	1	4.13	25	0.1	β,β'-ジメチルシステイン (ベニシラミン)	1	1.90	25	0.1
	2	5.03	25	0.1		2	7.88	25	0.1
o-クレゾール		10.28	25	0		3	10.58	25	0.1
m-クレゾール		10.09	25	0	2,6-ジメチルピリジン		6.90	25	0.5
p-クレゾール		10.26	25	0	シュウ酸	1	1.04	25	0.1
クロトン酸		4.69	25	0		2	3.82	25	0.1
o-クロロアニリン		2.64	25	0	d-酒石酸	1	2.82	25	0.1
m-クロロアニリン		3.34	25	0		2	3.95	25	0.1
p-クロロアニリン		3.99	25	0	(R,R)-酒石酸	1	2.99	25	0.1
chlorobenzene acid → o-クロロ安息香酸		2.92	25	0		2	4.44	25	0.1
m-クロロ安息香酸		3.82	25	0	セリン	1	2.13	25	0.1
p-クロロ安息香酸		3.99	25	0		2	9.06	25	0.1
クロロ酢酸		2.68	25	0.1	タウリン	2	8.95	25	0.5
o-クロロフェノール		8.29	25	0.1	チオフェノール		6.46	25	0.1
m-クロロフェノール		8.78	25	0.1	チロシン	1	2.17	25	0.1
p-クロロフェノール		9.14	25	0.1		2	9.04	25	0.1
2-クロロプロピオン酸		2.71	25	0.1		3	10.14	25	0.1
3-クロロプロピオン酸		3.92	25	0.1					

Transaction

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CHANGES IN ZETA POTENTIALS OF AMORPHOUS CELLULOSE PARTICLES WITH ALUMINUM SULFATE

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ABSTRACT: Microcrystalline cellulose powder, linter cellulose, softwood bleached kraft pulp (SBKP), and hardwood bleached kraft pulp (HBKP) were converted to amorphous particles, and ζ -potentials of suspended samples were measured with the addition of aluminium sulfate (alum). ζ -Potentials of these samples without alum were related to their carboxyl content, and the sample with higher carboxyl content has the more negative ζ -potential. In the presence of alum in suspensions, ζ -potentials are influenced not only by carboxyl content but also swelling degrees of samples. When amorphous samples with different swelling degrees were prepared from microcrystalline cellulose powder, the amorphous sample with higher swelling degree had the more negative ζ -potential. ζ -Potentials of amorphous particles prepared from linter cellulose, SBKP, and HBKP were shifted to positive direction by the addition of alum to suspensions, but never turned to positive over the wide range of alum addition. ζ -Potentials of amorphous particles prepared from linter cellulose, SBKP, and HBKP were almost unchanged at least for one day, during standing of suspensions at room temperature after the addition of alum. In contrast, ζ -potentials of microcrystalline cellulose powder and those of amorphous particles prepared from microcrystalline cellulose powder were shifted to negative direction by standing of suspensions. These relaxation phenomena of ζ -potentials in the presence of alum may depend on structural changes of alum in suspensions during the standing.

1. INTRODUCTION

Control of surface charges of pulp fibers and paper-additive in pulp suspension is significant process for papermaking. Since pulp fibers and most of sizing chemicals and fillers have negative ζ -potentials in aqueous suspensions, cationic compounds are used as retention aids for the paper components. Aluminium sulfate (alum) have been widely used as a retention aid primarily in acidic papermaking, and retention mechanism have been studied by using NMR and others [1-4]. Aluminium ion compresses ionic atmospheres and double layers on the surface of paper components, and thereby leads to a shift of ζ -potential to positive direction. Thus, this effect brings about an increase in flocculation force of the components by decreasing electrostatic repulsions [5]. The use of cationic polymers has been increasing in both acidic and alkaline papermaking, and electrostatic interactions between cationic polymers and cellulose surface have been studied [6-11].

Although interactions between cationic compounds and cellulose surface are complicated partly because of the swelling effects of cellulose in water, ζ -potentials of cellulose often provide good interpretation for understanding various electrokinetic phenomena in wet-end chemistry [12-16]. Electrophoresis of cellulose particles is one of the convenient methods for determining ζ -potentials of cellulose in the presence of additives. Since these electrokinetic phenomena take place by interactions between polysaccharides in non-crystalline regions of pulp fibers, water, and additives, properties of non-crystalline regions must have great influence on electrokinetic phenomena. Onabe and Nakano reported that decrystallization of pulp fibers with ethylene diamine, resulted in changes in ζ -potentials, which were determined by the stream current method [17]. These changes were explained in terms of changes in ion-adsorption properties at the surface of pulp fibers by the decrystallization.

In this paper, therefore, ζ -potentials of crystalline

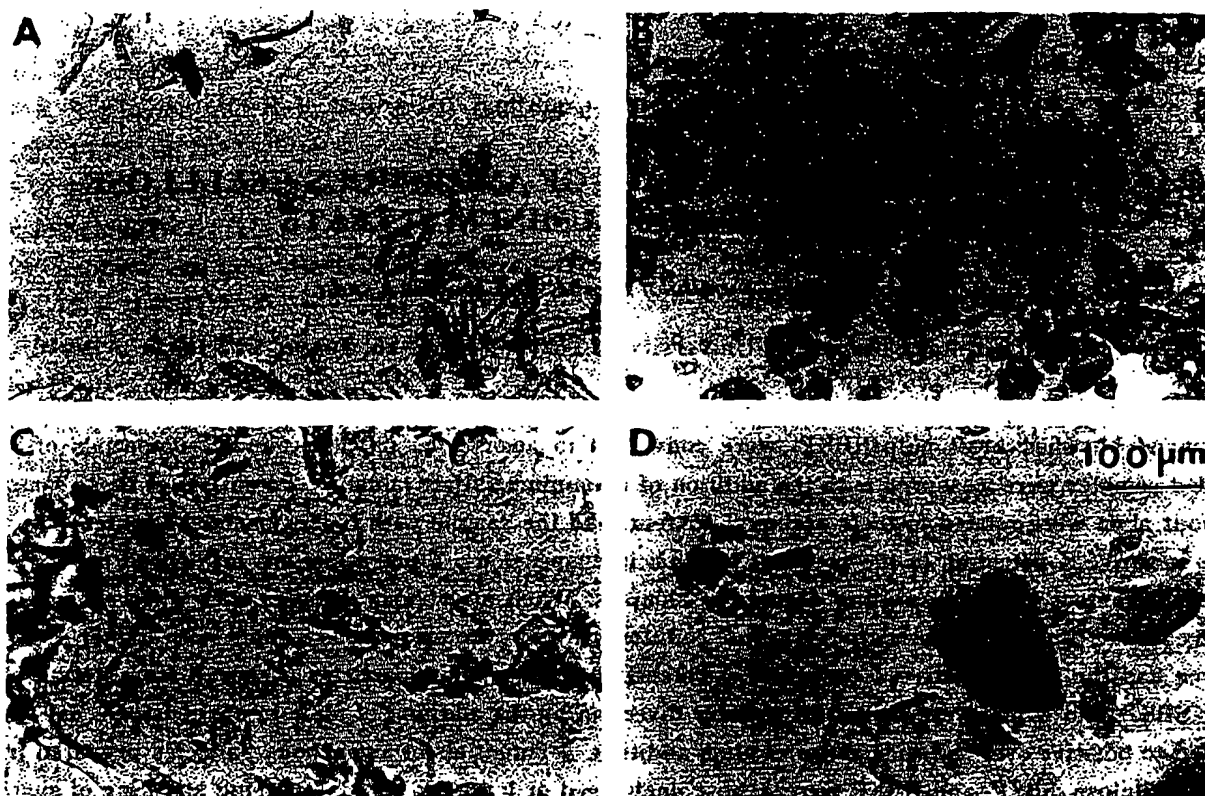


Fig. 1. Optical micrographs of suspensions of cellulose particles in water. (A); Microcrystalline cellulose powder, (B); oven-dried amorphous cellulose, (C); freeze-dried amorphous cellulose, and (D); never-dried amorphous cellulose gel.

and amorphous cellulose particles in the presence of alum were measured by the electrophoresis method, and interactions between alum and non-crystalline regions of pulp fibers were studied. This study has been conducted as a series of characterization of non-crystalline regions of cellulosic materials under aqueous conditions [18-22].

2. EXPERIMENTAL

2.1 Samples

Commercially available microcrystalline cellulose powder (Avicel, Asahi Chemical Co. Ltd., $DP_v = 200$), linter cellulose ($DP_v = 980$), and bleached kraft pulps prepared from softwood (SBKP, $DP_v = 880$) and hardwood (HBKP, $DP_v = 930$) were used as cellulose and wood pulp samples. Amorphous cellulose and amorphous pulp samples were prepared from the above cellulose and pulp samples according to the method reported previously [18-24]. The regenerated amorphous gels were converted to fine-particle gels by treating with a blender for one minute. These never-dried gels were used as the amorphous gel sam-

ples, and freeze-dried amorphous samples were prepared from the never-dried gels. Oven-dried amorphous samples were prepared from the fine-particle gels by washing thoroughly with methanol and acetone, and by drying *in vacuo*.

Carboxyl content of cellulose and pulp samples were measured according to TAPPI Test Methods [25].

2.2 Measurement of Zeta-potentials

A sample (50 mg by dry weight) was suspended in 50 mL of distilled water, and the suspension was left standing for one day for sufficient swelling. Then a designed amount of freshly-prepared aluminium sulfate solution was added to the suspension, and the suspension was vigorously shaken. ζ -Potentials of the particles were measured at 10 min, 3 h, and 1 day after the addition of aluminium sulfate, using a micro-electrophoresis apparatus (Mark II, Rank Brothers Co.) with a flat cell and a CD camera. Mobilities were obtained from average migration velocities of the particles in suspension at 25°C, and ζ -potentials were calculated from the mobilities, according to the

Helmholtz-Smoluchowski's equation [13].

3. RESULTS AND DISCUSSION

3.1 ζ -Potentials of Crystalline and Amorphous Celluloses

Fig. 1 shows optical microphotographs of microcrystalline cellulose powder, and oven-dried, freeze-dried, and never-dried amorphous cellulose samples. All amorphous samples were prepared from microcrystalline cellulose powder, and thus these samples had almost equal DPv values of 200 [23]. The never-dried sample had a fully swollen gel-form. The freeze-dried sample had the angular surface, and the oven-dried sample had the smooth one. Microcrystalline cellulose powder had the rectangular shape. Microcrystalline cellulose powder and oven-dried amorphous cellulose particles had relatively narrow distribution of shape and size among the samples used.

Figs. 2, 3, and 4 show ζ -potentials of microcrystalline cellulose powder and its amorphous samples, measured at 10 min, 3 h, and 1 day, respectively, after the addition of alum. ζ -Potentials of amorphous samples without alum were almost equal to one another, from -23 to -24 mV. Microcrystalline cellulose powder had a slightly more negative value, -26 mV, than the above values. This result indicates that ζ -

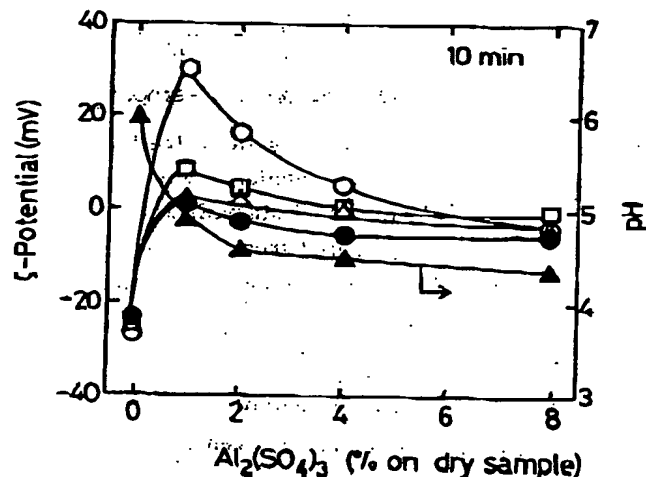


Fig. 2. ζ -Potentials of crystalline and amorphous cellulose samples with aluminium sulfate and pH (\blacktriangle) of supernatant. Measured at 10 min after the addition of aluminium sulfate. \circ ; Microcrystalline cellulose powder, \square ; oven-dried amorphous cellulose, \triangle ; freeze-dried amorphous cellulose, and \bullet ; never-dried amorphous cellulose gel. All samples had DPv of 200.

potentials of amorphous cellulose particles in distilled water are almost independent of particle shape, size, or swelling degrees. As described later, ζ -potentials of amorphous cellulose particles in distilled water were directly related to carboxyl content of samples.

On the other hand, ζ -potentials changed with various patterns by the addition of alum to the suspensions. Basically negative ζ -potentials were shifted to positive direction with an increased amount of alum, where pH values of suspensions decreased from 4.8 to 4.3 with the addition of alum from 1 to 8% on dry weight of cellulose samples. The shifting degrees of

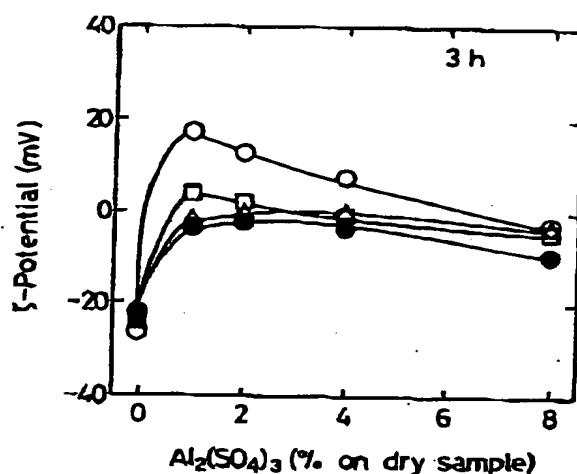


Fig. 3. ζ -Potentials of crystalline and amorphous cellulose samples in suspension with aluminium sulfate. Measured at 3 h after the addition of aluminium sulfate. See footnote in Fig. 2.

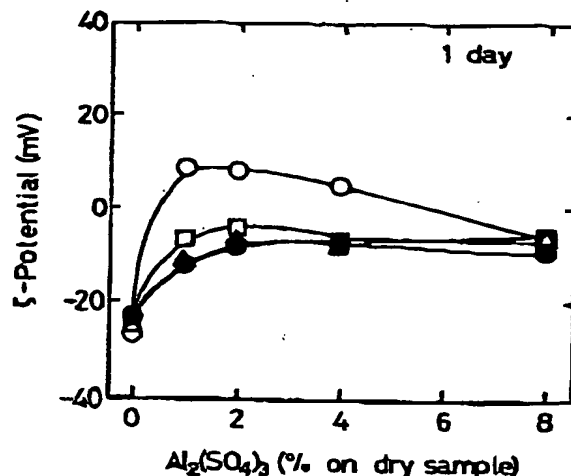


Fig. 4. ζ -Potentials of crystalline and amorphous cellulose samples in suspension with aluminium sulfate. Measured at 1 day after the addition of aluminium sulfate. See footnote in Fig. 2.

ζ -potentials were observed as the following order: microcrystalline cellulose powder > oven-dried amorphous cellulose particles \geq freeze-dried amorphous cellulose particles \approx never-dried amorphous cellulose gel particles. These effects of alum for shifting ζ -potentials of cellulose samples to positive direction are explained in terms of a decrease in $1/k$ (thickness of the ionic atmosphere) with an increase in aluminium ion [21]. However, microcrystalline cellulose powder had a large positive value, +30 mV, at 10 min after the 1% alum addition, and this phenomenon could not be explained simply in terms of the decrease in the $1/k$ value. Probably swelling degrees, crystallinities, and / or thickness of swelling layers of samples may have influence on the interactions with aluminium ion.

ζ -Potentials were slightly shifted to negative direction by standing of suspensions at room temperature for one day after the addition of alum, although pH values were unchanged during the standing. These relaxation phenomena of ζ -potentials may be explained in terms of re-distribution of aluminium ions on the swollen cellulose surface and / or some structural changes of alum, such as polymerization, formation of aluminium hydroxide, and others [1-4]. Since this relaxation behaviour was observed for all samples having different swelling degrees, the structural changes of alum are more plausible for explaining the results obtained in this study.

3.2 ζ -Potentials of Amorphous Pulps

Since most of linter cellulose and wood pulps have fibrous forms, they are unsuitable for determining ζ -potentials by electrophoresis. ζ -Potentials of their fine fractions can be subjected to electrophoresis, but fine fractions may not be representative of total fibers [12]. In this section, linter cellulose, SBKP, and HBKP fibers were converted to oven-dried amorphous particles by using a cellulose solvent system, and their ζ -potentials were measured in the presence of alum in order to characterize non-crystalline regions of these samples. The reasons to use oven-dried amorphous particles were as follows; 1) as described in the above section, amorphous samples prepared by different drying methods had similar ζ -potentials and relaxation patterns in the presence of alum, 2) the oven-dried amorphous particles were spherical and

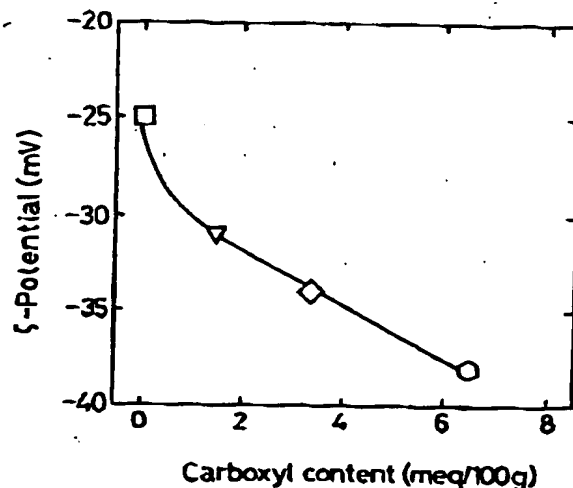


Fig. 5. Relationship between carboxyl content of original samples and ζ -potentials of the corresponding amorphous particles in distilled water. □; Microcrystalline cellulose powder, ▽; linter cellulose, ◇; SBKP, and ○; HBKP.

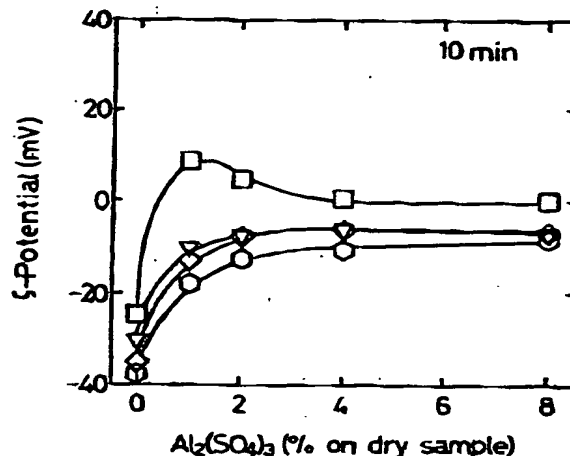


Fig. 6. ζ -Potentials of various oven-dried amorphous samples in suspension with aluminium sulfate. Measured at 10 min after the addition of aluminium sulfate. Amorphous samples were prepared from, □; microcrystalline cellulose powder, ▽; linter cellulose, ◇; SBKP, and ○; HBKP.

had relatively narrow distribution of ζ -potentials, shape, and particle size, and 3) oven-dried amorphous particles were easy for handling.

ζ -Potentials without alum were -25, -31, -34, and -38 mV for oven-dried amorphous particles prepared from microcrystalline cellulose powder, linter cellulose, SBKP, and HBKP, respectively. Fig. 5 shows relationship between the ζ -potentials and carboxyl content of the original samples. Clearly these amor-

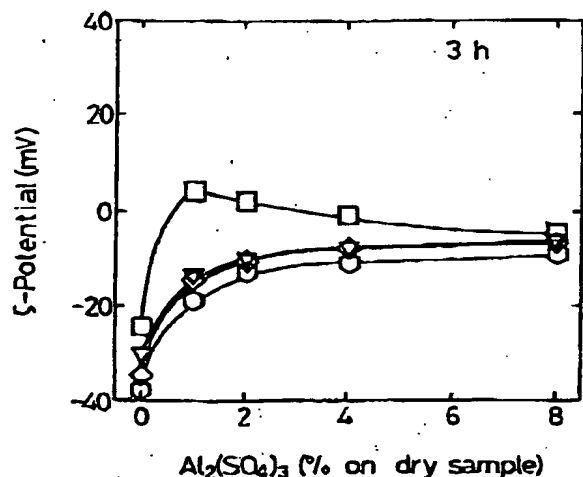


Fig. 7. ζ -Potentials of amorphous pulps and celluloses in suspension with aluminium sulfate. Measured at 3 h after the addition of aluminium sulfate. See footnote in Fig. 6.

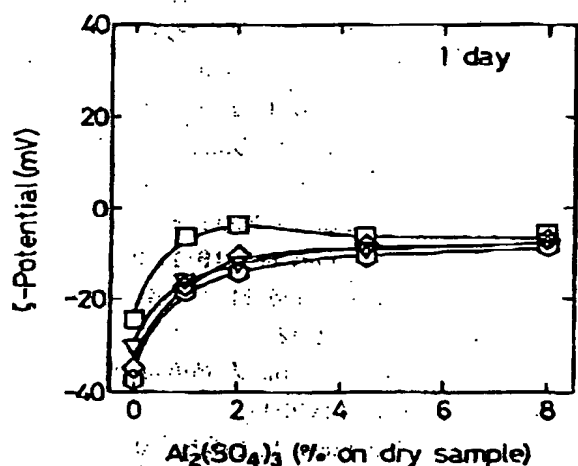


Fig. 8. ζ -Potentials of amorphous pulps and celluloses in suspension with aluminium sulfate. Measured at 1 day after the addition of aluminium sulfate. See footnote in Fig. 6.

phous samples had the more negative ζ -potentials with an increase in carboxyl content of the samples. Since linear relationship was observed for linter cellulose, SBKP, and HBKP, the relative values of ζ -potentials within this range in distilled water can be explained directly in terms of carboxyl content of samples.

Figs. 6, 7, and 8 show changes in ζ -potentials of oven-dried amorphous particles prepared from microcrystalline cellulose powder, linter cellulose, SBKP, and HBKP in the presence of alum at 10 min, 3 h, and 1 day, respectively, after the addition of alum to the

suspensions. ζ -Potentials of the amorphous particles prepared from linter cellulose, SBKP, and HBKP were negative all over the range of the alum addition from 0 to 8%, while these values were shifted to positive direction with the addition of alum. These three samples showed similar patterns of changes in ζ -potentials by the addition of alum, while the amorphous particles prepared from microcrystalline cellulose powder had a pattern different from those of other samples. This unique pattern may be explained in terms of the extremely low value of carboxyl content of microcrystalline cellulose powder; the low carboxyl content may cause the less swollen structure of the amorphous particles than those prepared from other samples. As described in the previous section, the swelling degrees of the particles had influence on changes in ζ -potentials with the addition of alum. Although it was found that electrokinetic phenomena are primarily governed by interactions between carboxyl groups and aluminium ions for cellulose samples, such as linter cellulose, SBKP, and HBKP, some other interactions must be present in electrokinetic phenomena for samples with extremely low or no carboxyl content. Therefore, in either case, carboxyl content of cellulose samples must have great influence on ζ -potentials in the presence of alum.

No relaxation phenomena of ζ -potentials of amorphous particles in the presence of alum were observed for linter cellulose, SBKP, and HBKP, which had ζ -potentials more negative than -5 mV even after the addition of alum. As described in the above section, some structural changes of alum seem to cause the relaxation phenomena of ζ -potentials of amorphous cellulose particles during standing of suspensions at room temperature. Thus, the negative ζ -potentials of non-crystalline regions in pulp fibers are shifted to positive direction with an increased amount of alum, but that the values are always negative. Furthermore, the negative values seem to be unchanged during standing of suspensions after the addition of alum.

In conclusion, ζ -potentials of cellulose and pulp samples were able to be compared by using their amorphous particles having similar shape and size; effects of differences in crystallinity, fiber size and shape, and other macroscopic factors of samples on

electrokinetic phenomena can be excluded by the method used in this study. The results obtained showed that carboxyl groups in non-crystalline regions of pulp fibers must play a significant role in electrokinetic phenomena or interactions between swollen cellulose surface and electrolytes under aqueous conditions.

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編



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f. 変質基 パルプの製造過程で加水分解あるいは酸化の作用が鎖状分子に及ぶと、鎖状分子の切断により還元性末端基が増加し、あるいは鎖状分子中の水酸基が酸化されてカルボニル基またはカルボキシル基が生成する。

還元性基の量を求めるために銅価が古くから測定されているが、銅価とはアルカリ溶液中で試料 100 g によって第二銅から第一銅に還元される銅の g 数をいい、カルボニル基量と化学量論的に直接的な関係はない。

JIS 法¹⁾では、試料 2.5 g を三角フラスコに入れて沸騰水浴中に深く浸し、15 分後に処理溶液と混合し、30 分ごとに振とうしながら冷却管をつけて3時間処理する。添加溶液は、A液 (1l 中に硫酸銅 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 100 g を含む) 5 cc ならびに B液 (1l 中に炭酸水素ナトリウム 50 g および炭酸ナトリウム 129 g を含む) 95 cc を使用直前に混合して加熱しておく。試料は熱いままガラスろ過器 (3G4 または 3G3) に移し、少量の熱 1% 炭酸ナトリウム溶液、熱水続いて冷水で洗浄したのち、C溶液 (1l 中に硫酸第二鉄アンモニウム $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ 100 g および 95% 硫酸 140 cc を含む) 25 cc を用いて酸化第一銅を溶解し、更に 10% 硫酸 200 cc 続いて冷水 100 cc で洗浄し、ろ洗液を 0.04 N 過マンガン酸カリウム溶液で滴定す

る。空試験との差から酸化第一銅で還元されて生成した第一鉄イオンによる過マンガン酸カリウム溶液の消費 cc 数 (V) を求め、次式から銅価を算出する。

$$\text{銅価} = 0.254 V / S \quad S: \text{試料重量}$$

なお、Lidman-Safwat および Theander²⁾ は次亜塩素酸処理パルプについて銅価とカルボニル基量との間に図 13.88 のような関係を認めている。

熱アルカリ溶解度もカルボニル基量とある程度相関するが、これは熱アルカリ溶液による溶解が炭水化物のカルボニル基を起点として起こり、溶出量が起点の

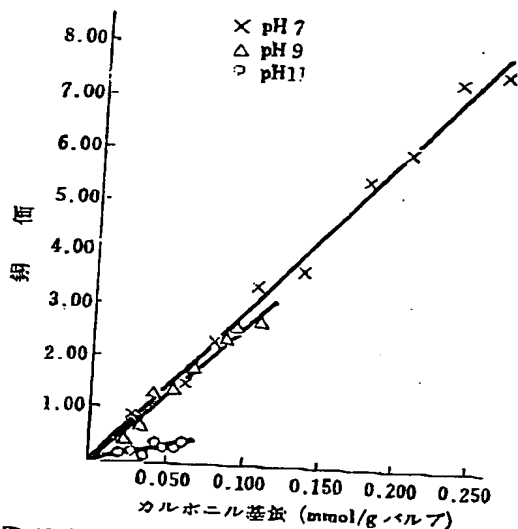


図 13.88 3 種の pH で次亜塩素酸酸化を行なったセルロースについて得た銅価とカルボニル基量の関係²⁾

1) JIS P 8101-1961.

2) S. Lidman-Safwat, O. Theander: Svensk Papperstidn., 61, 42 (1958).

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DECLARATION

I, Maemi NAKAMOTO, declare that I reside at 16-12, Misaki 5-chome, Suminoe-ku, Osaka-shi, OSAKA 559-0013 JAPAN;

That I am familiar with the English and Japanese languages;

That I have prepared a translation of Japanese Patent Application No. 66501/1998, "セルロースアセテートおよびそれを含むドープ, CELLULOSE ACETATE AND DOPE CONTAINING THE SAME"; said translation thereof being attached hereto and made a part of this declaration;

That to the best of my knowledge and belief, the attached translation is accurate and fairly reflects the contents and meaning of the foregoing Japanese language document.

I declare, under penalty of perjury under the laws of the United States of America, that the foregoing is true and correct.

Executed, on April 15, 1999.

Maemi Nakamoto

Maemi NAKAMOTO

PATENT OFFICE
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This is to certify that the annexed is a true copy
of the following application as filed with this Office.

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Application Number: 66501/1998
Applicant(s): Daicel Chemical Industries, Ltd.

August 14, 1998

Commissioner,
Patent Office

Takeshi Isayama

Certification No. 3065680/1998

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[Filing Date]	March 17, 1998
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[Item]	Abstract	one copy
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[Requirement of Proof] Yes

[Document Name] Specification

[Title of the Invention] CELLULOSE ACETATE AND DOPE
CONTAINING THE SAME

[Claims]

[Claim 1] A cellulose acetate having carboxyl groups binding to a cellulose acetate and/or a hemicellulose acetate, wherein at least a part of said carboxyl groups are in an acidic form.

[Claim 2] A cellulose acetate containing at least one member selected from the group consisting of an acid having an acid dissociation exponent pKa of 1.93 to 4.50 in water, an alkali metal salt of said acid and an alkaline earth metal salt of said acid.

[Claim 3] A cellulose acetate containing an alkali metal or an alkaline earth metal wherein the total content of an alkali metal and an alkaline earth metal in 1 gram of the cellulose acetate is from an effective amount to 5.5×10^{-6} equivalent (in terms of ion equivalent).

[Claim 4] A cellulose acetate containing at least one member selected from an acid dissociation exponent pKa of 1.93 to 4.50 in water, an alkali metal salt of said acid and an alkaline earth metal salt of said acid; and

having carboxyl groups binding to a cellulose acetate and/or a hemicellulose acetate, wherein at least a part of said carboxyl groups are in an acidic form.

[Claim 5] A cellulose acetate containing an alkali metal or an alkaline earth metal wherein the total content

of an alkali metal and an alkaline earth metal in 1 gram of the cellulose acetate is from an effective amount to 5.5×10^{-6} equivalent (in terms of ion equivalent); and

having carboxyl groups binding to a cellulose acetate and/or a hemicellulose acetate, wherein at least a part of said carboxyl groups are in an acidic form.

[Claim 6] A cellulose acetate containing at least one member selected from an acid dissociation exponent pKa of 1.93 to 4.50 in water, an alkali metal salt of said acid and an alkaline earth metal salt of said acid; and

containing an alkali metal or an alkaline earth metal wherein the total content of an alkali metal and an alkaline earth metal in 1 gram of the cellulose acetate is from an effective amount to 5.5×10^{-6} equivalent (in terms of ion equivalent).

[Claim 7] A cellulose acetate containing at least one member selected from an acid dissociation exponent pKa of 1.93 to 4.50 in water, an alkali metal salt of said acid and an alkaline earth metal salt of said acid;

containing an alkali metal or an alkaline earth metal wherein the total content of an alkali metal and an alkaline earth metal in 1 gram of the cellulose acetate is from an effective amount to 5.5×10^{-6} equivalent (in terms of ion equivalent); and

having carboxyl groups binding to a cellulose acetate and/or a hemicellulose acetate, wherein at least a part of said carboxyl groups are in an acidic form.

[Claim 8] A cellulose acetate according to any one of claims 3, 5 to 7, wherein the total content of an alkali metal and an alkaline earth metal in 1 gram of the cellulose acetate is from an effective amount to 2.5×10^{-6} equivalent (in terms of ion equivalent).

[Claim 9] A cellulose acetate according to any one of claims 3, 5 to 7, wherein the total content of an alkali metal and an alkaline earth metal in 1 gram of the cellulose acetate is from an effective amount to 1×10^{-6} equivalent (in terms of ion equivalent).

[Claim 10] A cellulose acetate according to any one of claims 2, 4, 6 to 9, wherein pKa value of said acid is 2.0 to 4.4.

[Claim 11] A cellulose acetate according to any one of claims 2, 4, 6 to 10, wherein the acid is at least one organic acid selected from an aliphatic monocarboxylic acid, an aliphatic polycarboxylic acid, a hydroxycarboxylic acid and an amino acid or derivatives thereof.

[Claim 12] A cellulose acetate according to any one of claims 2, 4, 6 to 10, wherein the acid is at least one organic acid selected from a saturated or unsaturated C_{1-3} monocarboxylic acid, a saturated or unsaturated C_{2-4} dicarboxylic acid, a C_{1-6} hydroxycarboxylic acid and an amino acid.

[Claim 13] A cellulose acetate according to any one of claims 2, 4, 6 to 10, wherein the acid is at least one

member selected from formic acid, haloacetic acid, halopropionic acid, acrylic acid, malonic acid, succinic acid, glutaric acid, fumaric acid, glycolic acid, lactic acid, malic acid, tartaric acid and citric acid.

[Claim 14] A cellulose acetate according to any one of claims 2, 4, 6 to 10, wherein the total content of the acid and the metal salt thereof is 1×10^{-3} to 3×10^{-5} relative to 1 gram of the cellulose acetate.

[Claim 15] A cellulose acetate according to any one of claims 2, 4, 6 to 10, wherein the total content of the acid and the metal salt thereof is 1×10^{-8} to 2×10^{-5} mole relative to 1 gram of the cellulose acetate.

[Claim 16] A cellulose acetate according to any one of claims 2, 4, 6 to 10, wherein the total content of the acid and the metal salt thereof is 1×10^{-7} to 1×10^{-5} mole relative to 1 gram of the cellulose acetate.

[Claim 17] A cellulose acetate according to any one of claims 1 to 16, which has the slurry pH of 4.5 to 5.5.

[Claim 18] A cellulose acetate according to any one of claims 1 to 16, which has the slurry pH of 4.8 to 6.0.

[Claim 19] A cellulose acetate according to any one of claims 1 to 18, which has the average degree of acetylation of 43.7 to 62.5%.

[Claim 20] A cellulose acetate according to any one of claims 1 to 19, which is produced by using sulfuric acid as a catalyst for acetylation and/or aging.

[Claim 21] A cellulose acetate according to any one

of claims 1 to 20, wherein a cellulose as raw material is at least one selected from a wood pulp and a linter pulp.

[Claim 22] A cellulose acetate according to any one of claims 1 to 21, wherein a cellulose as a raw material is at least one selected from a hardwood pulp and a softwood pulp.

[Claim 23] A dope containing at least one cellulose acetate recited in any one of claims 1 to 22.

[Claim 24] A dope containing (a) a cellulose acetate and (b) at least one member selected from an acid having a acid dissociation exponent pK_a of 1.93 to 4.50 in water, an alkali metal salt of the acid and an alkaline earth metal salt of the acid.

[Claim 25] A method for improving releasability of a film from a support or spinnability with using the dope according to claim 23 or 24.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

This invention relates to a cellulose acetate useful for the production of films (polarizer protective films, color filters, films for photosensitive materials) and fibers, and a dope containing the same.

[0002]

[Background Art]

Cellulose triacetate film is tough and has good dimensional stability, heat resistance, and optical

isotropy. Therefore, it has been used in various applications such as a substrate for optical thin-film devices (e.g. a substrate for photosensitive materials), a polarizer protective film (e.g. liquid crystal protective film) for liquid crystal devices, and color filters. Therefore, cellulose triacetate film is required to have satisfactory optical characteristics, for example, low yellowness index, haze, and birefringence and high transparency. When a solution (dope) containing cellulose acetate such as cellulose diacetate and a solvent is used in the production of fibers, it is required to have high spinnability.

[0003]

To assure satisfactory optical characteristics, the cellulose acetate film is generally produced by the technology which comprises acetylating a linter pulp, a softwood pulp or a hardwood pulp, casting a solution (dope) containing the resulting cellulose acetate and a solvent on a support, and releasing the resulting film from the support.

However, when a linter pulp is used, the cost of the cellulose acetate is inevitably high. Moreover, when a high-purity softwood pulp among softwood pulps is used, there is a problem with steady supply of a raw material. When a low-purity softwood pulp is used, a transparency of a cellulose acetate tends to decrease. On the other hand, a hardwood pulp generally is advantageous cost-wise but

is not satisfactory in the releasability of the cast film from the support so that it is difficult to attain a satisfactory surface smoothness and sufficiently high productivity. Furthermore, a cellulose acetate obtained from a low-purity pulp injures the stability of its dope or filterability and thus lowers the spinnability.

[0004]

[Problems to be Solved by the Invention]

It is, therefore, an object of the present invention to provide a cellulose acetate which insures good releasability from a support in a casting process, and a dope containing the same.

It is another object to provide a cellulose acetate with high releasability in a casting process as well as satisfactory optical properties, and a dope containing the same.

A further object of the invention is to provide a cellulose acetate with a high spinnability in the production of fibers with use of its dope, and a dope containing the same.

It is yet another object of the invention to provide a cellulose acetate with high releasability, excellent optical properties and spinnability as well as good heat resistance.

[0005]

[Means to Solve the Problems]

To accomplish the above objects, the inventors of

the present invention did much research and found that (I) the form of the carboxyl group binding to a cellulose acetate and/or hemicellulose acetate or (II) the content of an alkali metal or an alkaline earth metal in a cellulose acetate remarkably affects releasability and transparency of a film or spinnability of a dope. The present invention has been accomplished based on the above findings.

[0006]

Thus, the cellulose acetate of the present invention includes (1) a cellulose acetate wherein at least a part of carboxyl groups binding to a cellulose acetate and/or hemicellulose acetate are in the form of an acid (an acidic form), (2) a cellulose acetate containing at least one member selected from an acid having an acid dissociation exponent pKa of 1.93 to 4.50 in water, an alkaline metal salt of the acid and an alkaline earth metal salt of the acid, and (3) a cellulose acetate wherein the total content of an alkaline metal and an alkaline earth metal in 1 gram (1g) of the cellulose acetate is from an effective amount to 5.5×10^{-6} equivalent (in terms of ion equivalent).

Moreover, the cellulose acetate of the present invention includes a cellulose acetate combinationally having two or more features or characteristics selected from the above features or characteristics (1), (2) and (3).

Further, the present invention includes a cellulose acetate which is given heat resistance by adjusting the

slurry pH to 4.5 to 6.0 with use of the acid or salts thereof.

[0007]

A dope of the present invention contains at least one cellulose acetate among the cellulose acetates mentioned above. Moreover, the dope of the present invention includes a dope containing (a) a cellulose acetate, and (b) at least one member selected from an acid having a acid dissociation exponent pK_a of 1.93 to 4.50 in water, an alkaline metal salt of the acid and an alkaline earth metal salt of the acid.

Furthermore, the present invention includes a method for improving a releasability of a film from a support or a spinnability in the production of fibers, by using the above dope.

[0008]

Incidentally, in the case of a multistage-dissociative acid, the acid dissociation exponent pK_a is different according to a dissociation stage. In the specification, the meaning of "the acid dissociation exponent pK_a of 1.93 to 4.50" is that the acid dissociation exponent pK_a at least in the first stage (the dissociation stage 1) is the range of 1.93 to 4.50.

[0009]

[Preferred Embodiment of the Invention]

A cellulose acetate of the present invention can be produced by acetylating a pulp. The species of the pulp is not particularly limited, and may be used various pulps.

Typically, at least one pulp selected from a wood pulp (e.g., a hardwood pulp and a softwood pulp) and a linter pulp may be used, and the wood pulp and the linter pulp may be combinatorially used. The content of α -cellulose, which is an indicator of purity of a pulp, may be selected within the range of, for example, about 90 to 100% by weight, and practically about 92 to 98% by weight in a wood pulp. According to the present invention, a low-purity pulp such as a pulp having an α -cellulose content of about 90 to 97% by weight (in particular about 92 to 96% by weight) may be used. Among these pulps, the wood pulp is practically used. As described above, a cellulose acetate produced by using a hardwood pulp as a raw material is generally inferior in releasability of a film in the casting process, and a cellulose acetate produced by using a softwood pulp as a raw material is inferior in optical characteristics such as transparency, or spinnability. The present invention can improve releasability of a cellulose acetate film, optical characters such as transparency and spinnability of a cellulose acetate in spite of using the wood pulp as a raw material.

[0010]

The cellulose acetate can be produced by the conventional production technology, for example, the process using sulfuric acid as a catalyst, the acetic acid process, and the methylene chloride process. The cellulose acetate is usually produced by treating a

starting pulp (cellulose) with acetic acid or the like (activation step), acetylating the same with acetic anhydride in the presence of the sulfuric acid catalyst to give a cellulose triacetate (acetylation step), and hydrolyzing or aging the triacetate to adjust its degree of acetylation (saponification step, or ripening or aging step).

In this process, the activation step can be carried out by spraying a mist of acetic acid or aqueous acetic acid on the pulp (cellulose) or by dipping the pulp in an acetic acid or aqueous acetic acid bath. The amount of acetic acid relative to 100 parts by weight of the pulp (cellulose) is about 10 to 100 parts by weight, preferably about 20 to 80 parts by weight, and more preferably about 30 to 60 parts by weight.

The amount of acetic anhydride to be used in the acetylation step can be selected from a range conducive to the above-mentioned degree of acetylation. Thus, based on 100 parts by weight of the pulp (cellulose), the amount of acetic anhydride may for example be about 230 to 300 parts by weight, preferably about 240 to 290 parts by weight, and more preferably about 250 to 280 parts by weight.

In the acetylation step, acetic acid is generally used as the solvent. The amount of acetic acid to be used for this purpose may for example be about 200 to 700 parts by weight, preferably about 300 to 600 parts by weight, and more preferably about 350 to 500 parts by weight per

100 parts by weight of the pulp (cellulose).

As a catalyst for acetylation or aging, sulfuric acid is usually used. The amount of sulfuric acid relative to 100 parts by weight of cellulose is generally about 1 to 15 parts by weight, preferably about 5 to 15 parts by weight, and more preferably about 5 to 10 parts by weight. The saponification step or aging (or ripening) step can be carried out, for example, at a temperature of about 50 to 70°C.

[0011]

In order to improve the optical characteristics of a cellulose acetate, treatment of a cellulose acetate with an oxidizing agent may be conducted in a suitable stage of production, for example, after the acetylation reaction or after the saponification (hydrolysis) reaction or aging. The oxidizing agent includes, but is not limited to, hydrogen peroxide; peracids such as performic acid, peracetic acid and perbenzoic acid; and organic peroxides such as diacetyl peroxide and so forth. The oxidizing agents can be used singly or in combination. The preferred oxidizing agent is one which can be easily removed from the cellulose acetate without leaving any appreciable residues, thus including hydrogen peroxide, performic acid and peracetic acid. Particularly preferred are hydrogen peroxide and peracetic acid. The amount of the oxidizing agent can be selected according to the required optical parameter levels and, based on 100 parts by weight of

cellulose acetate, may for example be about 0.01 to 5 parts by weight, preferably about 0.1 to 2.5 parts by weight, and particularly about 0.1 to 1 parts by weight.

The treatment with the oxidizing agent can be carried out at a temperature suited to the oxidizing agent, for example, about 20 to 100°C, and preferably about 30 to 70°C.

[0012]

The average degree of acetylation of a cellulose acetate may be selected within the range of about 30 to 62.5% in accordance with applications or characteristics. Cellulose diacetate or cellulose triacetate is usually advantageous for commercial production. The average degree of acetylation of a cellulose acetate is, for example, about 43.7 to 62.5% (the average degree of substitution of an acetyl group: about 1.7 to 3.0), preferably about 45 to 62.5% (the average degree of substitution: about 1.8 to 3.0) and more preferably about 48 to 62.5% (the average degree of substitution: 2.0 to 3.0). In a cellulose triacetate, the average degree of acetylation is, for example, about 58 to 62.5%, preferably about 58.5 to 62% and more preferably about 59 to 62% (e.g., about 60 to 61%) for improved dimensional stability, moisture resistance and heat resistance.

[0013]

The degree of acetylation represents the amount of acetic acid bound and is the weight percentage of bound acetic acid per weight of cellulose unit. The degree of

acetylation can be determined in accordance with the procedure for determination of the degree of acetylation as set forth in ASTM D-817-91 (test methods for cellulose acetate etc.). The test protocol is as follows. Weigh exactly 1.9 g of cellulose acetate, previously dried, dissolve in 150 ml of a mixture of acetone-dimethyl sulfoxide (4:1, v/v), add 30 ml of an aqueous 1N-sodium hydroxide solution, and saponify at 25°C for 2 hours. Add phenolphthalein as an indicator and titrate the excess sodium hydroxide with 1N-sulfuric acid (concentration factor: F). Perform a blank test in the same manner and calculate the degree of acetylation by means of the following equation.

$$\text{Degree of acetylation (\%)} = [6.5 \times (B - A) \times F] / W$$

wherein A represents an amount of 1N-sulfuric acid (ml) added to the sample, B represents an amount of 1N-sulfuric acid (ml) added to blank, F shows a concentration factor of 1N-sulfuric acid, and W is a weight of the sample.

[0014]

The degree of polymerization of cellulose acetate, in terms of viscosity average degree of polymerization, is about 200 to 400, preferably about 250 to 400, and more preferably about 270 to 400 (e.g., about 290 to 400). Usually, the viscosity average degree of polymerization is about 270 to 350.

The average degree of polymerization can be

determined by the intrinsic viscosity method of Uda et al. (Kazuo Uda & Hideo Saito: Journal of the Society of Fiber Science and Technology, Japan, Vol. 18, No. 1, 105-120, 1962). In the method, a solvent may be selected according to the degree of acetylation of a cellulose acetate. For example, in the case of a cellulose triacetate, the test protocol is as follows. Dissolve cellulose triacetate in a mixture of methylene chloride-methanol (9:1, by weight) at a predetermined concentration c (2.00 g/L). Then, inject the solution into an Ostward viscosimeter and measure the flow time (in seconds) t of the solution between the viscosimeter graduations at 25°C. On the other hand, measure the blank flow time (in seconds) t_0 with the above solvent mixture and calculate the viscosity average degree of polymerization by means of the following formula.

$$\eta_{rel} = t/t_0$$

$$[\eta] = (\ln \eta_{rel})/c$$

$$DP = [\eta]/(6 \times 10^{-4})$$

wherein t shows a flow time (in seconds) of the solution, t_0 shows a flow time (in seconds) of the solvent, c represents a cellulose triacetate concentration of the solution (g/L), η_{rel} represents a relative viscosity, $[\eta]$ is an intrinsic viscosity, and DP is an average degree of polymerization.

When methylene chloride-methanol= 9/1 (by weight) is used as the solvent mixture, for instance, the viscosity of a 6 weight % solution of cellulose triacetate may for

example be about 200 to 700 cps, preferably about 250 to 600 cps, and particularly about 250 to 500 cps.

[0015]

For enhanced stability, such cellulose acetate contains a heat stabilizer such as an alkali metal (e.g., lithium, potassium, sodium), a salt or a compound thereof, and an alkaline earth metal (e.g., calcium, magnesium, strontium, barium), a salt or a compound thereof.

[0016]

The cellulose acetate of the present invention is mainly classified into the following three series or embodiments (1) to (3):

(1) a cellulose acetate wherein at least a part of carboxyl groups binding to a cellulose acetate and/or hemicellulose acetate are in an acidic form;

(2) a cellulose acetate containing at least one member selected from an acid having a acid dissociation exponent pK_a of 1.93 to 4.50 in water, an alkali metal salt of the acid and an alkaline earth metal salt of the acid; and

(3) a cellulose acetate wherein the total content of an alkali metal and an alkaline earth metal in 1 gram (1g) of the cellulose acetate is from an effective amount to 5.5×10^{-6} equivalent (in terms of ion equivalent).

[0017]

Moreover, the cellulose acetate of the present invention includes the following cellulose acetates (4)

to (7) selected from the combinations of the above series or embodiments (1) to (3).

(4) a combination of (1) and (2) mentioned above, i.e. a cellulose acetate containing at least one member selected from an acid having an acid dissociation exponent pKa of 1.93 to 4.50 in water, an alkaline metal salt of the acid and an alkaline earth metal salt of the acid, and wherein at least a part of carboxyl groups binding to a cellulose acetate and/or hemicellulose acetate are in the form of an acid.

(5) a combination of (1) and (3), i.e. a cellulose acetate wherein the total content of an alkaline metal and an alkaline earth metal in 1 gram of the cellulose acetate is from an effective amount to 5.5×10^{-6} equivalent (in terms of ion equivalent), and at least a part of carboxyl groups binding to a cellulose acetate and/or hemicellulose acetate are in the form of an acid.

[0018]

(6) a combination of (2) and (3), i.e. a cellulose acetate containing at least one member selected from an acid having an acid dissociation exponent pKa of 1.93 to 4.50 in water, an alkaline metal salt of the acid and an alkaline earth metal salt of the acid, and wherein the total content of an alkaline metal and an alkaline earth metal in 1 gram of the cellulose acetate is from an effective amount to 5.5×10^{-6} equivalent (in terms of ion equivalent).

(7) a combination of (1), (2) and (3), i.e. a cellulose acetate containing at least one member selected from an acid having an acid dissociation exponent pKa of 1.93 to 4.50 in water, an alkaline metal salt of the acid and an alkaline earth metal salt of the acid, wherein the total content of an alkaline metal and an alkaline earth metal in 1 gram of the cellulose acetate is from an effective amount to 5.5×10^{-6} equivalent (in terms of ion equivalent), and at least a part of carboxyl groups binding to a cellulose acetate and/or hemicellulose acetate are in the form of an acid.

[0019]

[The cellulose acetates of the embodiments (1), (4), (5) and (7)]

In the cellulose acetates of the embodiments (1), (4), (5) and (7), at least a part of carboxyl groups binding to a cellulose acetate and/or hemicellulose acetate are in the form of a free acid, and all of the carboxyl groups do not form a metal salt (e.g., the alkali metal salt or an alkaline earth metal salt of a carboxyl group). In the preferred cellulose acetate, the total carboxyl groups bound to a cellulose acetate and/or hemicellulose acetate contains at least about 30 mole%, preferably about 50 to 100 mole% and practically about 70 to 100 mole% of a free carboxyl group in the carboxyl groups.

[0020]

[The cellulose acetates of the embodiments (2), (4), (6)

and (7)]

In the cellulose acetates of the embodiments (2), (4), (6) and (7), an acid having an acid dissociation exponent pKa of 1.93 to 4.50 [preferably about 2.0 to 4.4, more preferably about 2.2 to 4.3 (e.g., about 2.5 to 4.0) and practically about 2.6 to 4.3 (e.g., about 2.6 to 4.0)] includes an inorganic acid and an organic acid. As pKa value of an acid, see "Chemical Handbook third revised edition, the basic chapter II" (edited by Japanese Chemical, published by Maruzen; Japan). Examples of the acid and the acid dissociation exponent pKa in parentheses are represented as follows.

[0021]

The inorganic acid includes, for example, HClO_2 (2.31), HOCN (3.48), molybdric acid (H_2MoO_4 : 3.62), HNO_2 (3.15), phosphoric acid (H_3PO_4 : 2.15), tripolyphosphoric acid ($\text{H}_5\text{P}_3\text{O}_{10}$: 2.0) and vanadic acid (H_3VO_4 : 3.78).

[0022]

Examples of the organic acid include an aliphatic monocarboxylic acid [e.g., formic acid (3.55); an acetic acid having a substituent such as oxalacetic acid (2.27), cyanoacetic acid (2.47), phenylacetic acid (4.10), phenoxyacetic acid (2.99), fluoroacetic acid (2.59), chloroacetic acid (2.68), bromoacetic acid (2.72), iodoacetic acid (2.98), mercaptoacetic acid (3.43) and vinylacetic acid (4.12); a halopropionic acid such as chloropropionic acid (2.71 to 3.92); 4-aminobutanoic acid

(4.03); acrylic acid (4.26)], an aliphatic polycarboxylic acid [e.g., malonic acid (2.65), succinic acid (4.00), glutalic acid (4.13), adipic acid (4.26), pimelic acid (4.31), azelaic acid (4.39), fumaric acid (2.85)], a hydroxycarboxylic acid [e.g., glycollic acid (3.63), lactic acid (3.66), malic acid (3.24), tartaric acid (2.82 to 2.99), citric acid (2.87)], an aldehyde acid or a ketone acid [e.g., glyoxylic acid (3.18), pyruvic acid (2.26), levulinic acid (4.44)], an aromatic monocarboxylic acid [e.g., anilinesulfonic acid (3.74 to 3.23); benzoic acid (4.20); a benzoic acid having a substituent such as aminobenzoic acid (2.02 to 3.12), chlorobenzoic acid (2.92 to 3.99), cyanobenzoic acid (3.60 to 3.55), nitrobenzoic acid (2.17 to 3.45), hydroxybenzoic acid (4.08 to 4.58), anisic acid (4.09 to 4.48), fluorobenzoic acid (3.27 to 4.14), chlorobenzoic acid, bromobenzoic acid (2.85 to 4.00) and iodobenzoic acid (2.86 to 4.00); salicylic acid (2.81); naphtoic acid (3.70 to 4.16); cinnamic acid (3.88); mandelic acid (3.19)], an aromatic polycarboxylic acid [e.g., phtalic acid (2.75), isophtalic acid (3.50), terephyhalic acid (3.54)], a heterocyclic monocarboxylic acid [e.g., nicotinic acid (2.05), 2-furancarboxylic acid (2.97)], and a heterocyclic polycarboxylic acid [e.g., 2.6-pyridinedicarboxylic acid (2.09)].

[0023]

The organic acid includes amino acids [i.e., an amino acid or derivative thereof (e.g., an amino acid having a

substituent, a peptide composed of about 2 to 5 amino acids).

The group of an amino acid includes, for example, an amino acid [e.g., asparagine (2.14), aspartic acid (1.93), adenine (4.07), alanine (2.30), β -alanine (3.53), arginine (2.05), isoleucine (2.32), glycine (2.36), glutamine (2.17), glutamic acid (2.18), serine (2.13), tyrosine (2.17), tryptophan (2.35), threonine (2.21), norleucine (2.30), valine (2.26), phenylalanine (2.26), methionine (2.15), lysine (2.04), leucine (2.35)], an amino acid derivative [e.g., adenosine (3.50), adenosine triphosphate (4.06), adenosine monophosphate (3.65 to 3.80), L-alanyl-L-alanine (3.20), L-alanylglycine (3.10), β -alanylglycine (3.18), L-alanylglycylglycine (3.24), β -alanylglycylglycine (3.19), L-alanylglycylglycylglycine (3.18), glycyl-L-alanine (3.07), glycyl- β -alanine (3.91), glycylglycyl-L-alanine (3.18), glycylglycylglycine (3.20), glycylglycylglycylglycine (3.18), glycylglycyl-L-histidine (2.72), glycylglycylglycyl-L-histidine (2.90), glycyl-DL-histidylglycine (3.26), glycyl-L-histidine (2.54), glycyl-L-leucine (3.09), γ -L-glutamyl-L-cysteinylglycine (2.03), N-methylglycine (sarcosine, 2.20), N,N-dimethylglycine (2.08), citrulline (2.43), 3,4-dihydroxyphenylalanine (2.31), L-hystidylglycine (2.84), L-phenylalanylglycine (3.02), L-prorylglicine (3.07), L-leuciyl-L-tyrosine (3.15)].

[0024]

As an acid, an organic acid such as an aliphatic monocarboxylic acid [e.g., formic acid, a haloacetic acid such as chloroacetic acid, a saturated or unsaturated C₁₋₃ monocarboxylic acid such as a halopropionic acid and acrylic acid], an aliphatic polycarboxylic acid [e.g., a saturated or unsaturated C₂₋₄ dicarboxylic acid such as malonic acid, succinic acid, glutalic acid and fumaric acid], a hydroxycarboxylic acid [e.g., C₁₋₆ hydroxycarboxylic acid such as glycollic acid, lactic acid, malic acid, tartaric acid and citric acid], and an amino acid or derivative thereof is practically used.

These acids may be water-insoluble or water-soluble.

[0025]

The acid may be used in the form of a free acid, or alkali metal salt or alkaline earth metal salt. The alkali metal includes, for example, lithium, potassium and sodium. The alkaline earth metal includes, for example, calcium, magnesium, barium and strontium. The preferred alkali metal includes sodium, and the preferred alkaline earth metal includes calcium and magnesium. Each of these alkali metals and alkaline earth metals may be used singly or in combination of two or more. A combination of the alkali metal and the alkaline earth metal may be used.

[0026]

The total content of the acid and metal salt thereof may be selected within the range not interfering with

releasability, transparency or spinnability, and may be about 1×10^{-9} to 3×10^{-5} mole, preferably about 1×10^{-8} to 2×10^{-5} mole (e.g., about 5×10^{-7} to 1.5×10^{-5} mole), more preferably about 1×10^{-7} to 1×10^{-5} mole (e.g., about 5×10^{-6} to 8×10^{-6} mole), and practically about 5×10^{-7} to 5×10^{-6} mole (e.g., about 6×10^{-7} to 3×10^{-6} mole) per 1g (gram) of a cellulose acetate.

[0027]

Incidentally, the content of the acid and metal salt thereof in a cellulose acetate may be quantitated as follows.

[Ion chromatography analysis]

A dried cellulose acetate (2.0g) in the form of minute powder is precisely weighed. To the cellulose acetate, 80ml of heated water is added and the resulting mixture is stirred and sealed. After standing over night, the mixture is further stirred and precipitated. As the sample solution, about 10 ml of supernatant is obtained. The content of the acid and the metal salt thereof is measured by ion chromatography.

[0028]

[The cellulose acetates of the embodiments (3), (5), (6) and (7)]

In the cellulose acetates of the embodiments (3), (5), (6) and (7), the total content of an alkali metal and an alkaline earth metal in 1 gram (1g) of the cellulose acetate is decreased in order to improve releasability of

a film in the casting process, transparency and spinnability.

An alkali metal and an alkaline earth metal include an alkali metal and an alkaline earth metal similar to those exemplified above. A cellulose acetate may contain either of an alkali metal or alkaline earth metal, or may contain both an alkali metal and alkaline earth metal.

[0029]

When the content of an alkali metal or alkaline earth metal is low, the alkali metal and/or alkaline earth metal may be bound to an acidic group (e.g., a carboxyl group, sulfonic acid group) of cellulose acetate. The total content of an alkali metal and alkaline earth metal in 1 gram of a cellulose acetate may be effective amount or more not interfering with heat resistance of the cellulose acetate, and may be about 5.5×10^{-6} equivalent or less (e.g., about 0.01×10^{-6} to 5×10^{-6} equivalent), preferably about 3.5×10^{-6} equivalent or less (e.g., about 0.01×10^{-6} to 3×10^{-6} equivalent) and more preferably about 2.5×10^{-6} equivalent or less (e.g., about 0.01×10^{-6} to 2×10^{-6} equivalent) in terms of ion equivalent. In particular, when the total content of an alkali metal and alkaline earth metal in 1 gram of a cellulose acetate is about 1.0×10^{-6} equivalent or less (e.g., about 0.1×10^{-6} to 0.5×10^{-6} equivalent) and practically about 0.3×10^{-6} equivalent or less (e.g., about 0.1×10^{-6} to 0.3×10^{-6} equivalent), the releasing resistance of a semi-dried film from a support

after casting a dope containing such cellulose acetate on the support by casting process can be decreased on releasing.

Incidentally, the content of an alkali metal and alkaline earth metal in a cellulose acetate may be quantitated by an atom absorptiometric analysis.

[0030]

Cellulose acetates of the embodiments (1) and (2) can be produced, for example, by mixing a cellulose acetate and an acid having the above acid dissociation exponent pK_a or metal salt thereof, or treating a cellulose acetate with the acid or metal salt thereof. The mixing or treatment of a cellulose acetate with the acid or metal salt thereof may be carried out in any steps, for example, during or after the production step of a cellulose acetate (e.g., an adding step of heat stabilizer after hydrolysis or aging step). Moreover, the treatment with the acid or metal salt thereof may be carried out by washing, dipping or immersing of a cellulose acetate in the form of particle or flake. Further, the mixing or treatment may be carried out by adding the acid or metal salt thereof to a dope containing a cellulose acetate.

The mixing or treatment with the acid having the above acid dissociation exponent pK_a or metal salt thereof may be carried out at a temperature not adversely affecting operatability, for example, about 10 to 70°C (preferably about 15 to 50°C). The mixing or treating time may be

selected within a broad range of, for example, about 1 minute to 12 hours.

At least a part of carboxyl groups binding to a cellulose acetate and/or hemicellulose acetate can become in the form of a free acid by using the acid having such acid dissociation exponent pK_a or metal salt thereof.

[0031]

The cellulose acetate of the embodiment (3) can be produced, for example, in the production process of the cellulose acetate by reducing the addition amount of a heat stabilizer (an alkaline metal salt or an alkaline earth metal salt) to the cellulose acetate, or treating a cellulose acetate with the acid having the above acid dissociation exponent pK_a or a metal salt thereof as described above.

[0032]

The cellulose acetate of the embodiment (4), i.e. a cellulose acetate having a carboxyl group in the form of an acid (embodiment (1)) and containing the acid having a specific acid dissociation exponent pK_a or a metal salt thereof (embodiment (2)) can be produced by incorporating the specific acid or metal salt thereof into a cellulose acetate by mixing (addition) or treatment to become at least a part of carboxyl groups binding to a cellulose acetate and/or hemicellulose acetate in the form of an acid (the formation of free carboxyl groups).

[0033]

The cellulose acetate of the embodiment (5), i.e. a cellulose acetate having a carboxyl group in the form of an acid (free carboxyl groups; embodiment (1)) and containing the reduced content of an alkali metal or an alkaline earth metal (embodiment (3)) can be produced by adjusting the additive amount of a heat stabilizer (an alkali metal salt or an alkaline earth metal salt) to a cellulose acetate, mixing the salt of the acid having pKa mentioned above (a salt of an alkali metal or an alkaline earth metal) to a cellulose acetate, or treating a cellulose acetate with the metal salt of the acid.

[0034]

The cellulose acetate of the embodiment (6), i.e. a cellulose acetate containing the acid having such acid dissociation exponent pKa or metal salt thereof (embodiment (2)) and having the reduced content of an alkali metal or an alkaline earth metal (embodiment (3)) can be produced by (i) adjusting the additive amount of the acid having the specific pKa or metal salt thereof, or (ii) adjusting the additive amount of the acid having the specific pKa or metal salt thereof, and of an alkali metal and/or an alkaline earth metal.

[0035]

The cellulose acetate of the embodiment (7), i.e., a cellulose acetate having a carboxyl group in the form of an acid (embodiment (1)), containing the acid having such acid dissociation exponent pKa or metal salt thereof

(embodiment (2)), and decreasing the content of an alkali metal or an alkaline earth metal (embodiment (3)) can be produced by (i) adjusting the adductive amount of the acid having the specific pKa or metal salt thereof by means of mixing (adding) or treatment, or (ii) adjusting the adductive amount of the acid having the specific pKa or metal salt thereof, and of an alkali metal and/or an alkaline earth metal.

[0036]

Such cellulose acetates have high releasability from a support in the production of a film by casting process, and improve a film-forming speed and productivity of a cellulose acetate film. Moreover, a cellulose acetate is superior in optical characteristics such as transparency. The transparency of a cellulose acetate is, for example, about 60 to 100% (preferably about 70 to 100%, and more preferably about 75 to 100%) and practically about 70 to 90%. The haze of the cellulose acetate is, for example, about 1 to 8 (preferably about 1 to 5). Further, the yellowness index (YI), which is an indicator of yellowness of a cellulose acetate, is for example, about 1 to 10 (preferably about 1 to 7 and practically about 2 to 5).

The transparency, haze, and yellowness index (YI) may be determined as follows.

[0037]

[Transparency]

Weigh exactly 8.0 g of cellulose acetate, previously

dried, add 125.3 g of a solvent (e.g., a mixture of methylene chloride-methanol (9:1, w/w) or acetone), and effect thorough dissolution (sample solution having a concentration of 6% (by weight)).

Using an AKA photoelectric colorimeter equipped with a cesium photoelectric tube and a filter No. 12, put the solvent in the glass cell with a light path length of 100 mm and measure the blank transmittance. Then, put the 6% (by weight) sample solution in the glass cell with a light path length of 100 mm and measure its transmittance. With the blank transmittance value being taken as 100%, the percentage of the transmittance value of the sample solution is recorded as the transparency of the sample.

[0038]

[Haze]

Weigh exactly 12.0 g of cellulose acetate, previously dried, add 88.0 g of a solvent (e.g., a mixture of methylene chloride-methanol (9:1, w/w) or acetone), and effect thorough dissolution (sample solution having a concentration of 12% (by weight)).

Using a turbidimeter (Nippon Denshoku Kogyo Co., Ltd.) and a glass cell (45 mm wide, 45 mm high, light path length 10 mm), perform measurements as follows.

Put the solvent in the glass cell, set the cell in the turbidimeter, and perform zeroing and calibration. Then, put the 12% (by weight) sample solution in the glass cell, set the cell in the turbidimeter, and record the

reading.

[0039]

[Yellowness Index (YI)]

Weigh exactly 12.0 g of cellulose acetate, previously dried, add 88.0 g of a solvent (e.g., a mixture of methylene chloride-methanol (9:1, w/w) or acetone), and effect thorough dissolution (a solution in a concentration of 12% by weight).

Using a color difference meter (Nippon Denshoku Kogyo Co., Ltd., Color Difference Meter Σ90) and a glass cell (45 mm wide, 45 mm high; light path length 10 mm), perform measurements and calculate YI by means of the following equation.

$$YI = YI_2 - YI_1$$

wherein YI_1 represents YI for the solvent, and YI_2 shows YI for the 12% (by weight) sample solution.

Further, the above cellulose acetates have a high solution stability, filterability and spinnability, and thus remarkably reduce the frequency of thread breakage in a continuous spinning for a long time.

[0040]

Furthermore, a cellulose acetate, which have high releasability, excellent optical characteristics and spinnability as well as high thermal-stability, can be obtained by adjusting a flake slurry pH to 4.5 to 6.0 with the acid or salt thereof according to the present invention.

The slurry pH is determined as follows.

[0041]

[Slurry pH]

Weigh exactly 2.0 g of cellulose acetate, previously dried in the form of minute powder, add 80 ml of a boiled distilled water, stir and seal. After standing over night, the mixture is stirred and precipitated. As the sample solution, about 10 ml of supernatant is obtained, and measured pH of the sample solution by means of pH meter corrected. As blank pH, the pH of the boiled distilled water is measured. The hydrogen ion concentration $[H^+]_s$ and $[H^+]_b$ (s: sample solution, b: blank solution) of the sample solution and the blank solution are calculated respectively by means of the calculation equation $[H^+] = 10^{-(pH)}$ (pH represents a pH value measured). In the case of $[H^+]_s \geq [H^+]_b$, the slurry pH may be calculated by the following formula:

$$\text{slurry pH} = -\log([H^+]_s - [H^+]_b)$$

In the case of $[H^+]_s < [H^+]_b$, the hydroxyl group ion-concentration $[OH^-]_s$ and $[OH^-]_b$ of the sample solution and the blank solution are calculated respectively by means of the calculation equation $[OH^-] = 10^{-14} \div [H^+]$. The slurry pH may be calculated by the following formula:

$$\text{slurry pH} = 14 + \log([OH^-]_s - [OH^-]_b + 10^{-7})$$

The cellulose triacetate can be produced by adjusting the concentration of the acid and/or salt thereof in the treatment step (washing or dipping step) of cellulose acetate (e.g., cellulose acetate in the form of particulate

or flake) and adjusting the pH of the aqueous slurry solution. Incidentally, the "treatment" may be carried out in any steps during or after the production of cellulose acetate.

[0042]

The cellulose acetate of the present invention having such characteristics is useful for the production of a film or fiber by using the solution (dope) containing the cellulose acetate. (I) The dope of the present invention contains at least one cellulose acetate of the above embodiments (1) to (7). (II) The another dope of the present invention contains (a) a cellulose acetate and (b) at least one member selected from an acid having a acid dissociation exponent pK_a of 1.93 to 4.50 in water, an alkaline metal salt of the acid and an alkaline earth metal salt of the acid. In the latter dope (II), (a) cellulose acetate may be any cellulose acetates of the embodiments (1) to (7), or other cellulose acetates than the cellulose acetates of the embodiments (1) to (7). That is, the other cellulose acetate wherein a carboxyl group binding to cellulose acetate and/or hemicellulose acetate is not in the form of acid but salt (an alkali metal salt, an alkaline earth metal salt), or a cellulose acetate containing the total content of an alkali metal and an alkaline earth metal is more than 5.5×10^{-6} equivalent per 1 gram in the term of ion equivalent may be used. The average degree of acetylation or the degree of polymerization of such

cellulose acetate may be selected within the range similar to that of the cellulose acetate of the present invention.

[0043]

The dope usually comprises a cellulose acetate and a solvent (an organic solvent). The solvent mentioned above may be selected according to the average degree of acetylation of the cellulose acetate and other factors, and include, for example, halogenated hydrocarbons (e.g., methylene chloride, ethylene chloride), ketones (e.g., acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone), esters (e.g., formic acid esters such as ethyl formate, acetic acid esters such as methyl acetate and ethyl acetate, ethyl lactate), ethers (e.g., dioxane, dimethoxyethane), cellosolves (e.g., methylcellosolve, ethylcellosolve), cellosolve acetates (e.g., methylcellosolve acetate, ethylcellosolve acetate), and a mixture of such solvents. The solvent may contain nitro compounds (e.g., nitromethane, nitroethane, nitropropane) and/or lower alcohols (e.g., methanol, ethanol, isopropanol, butanol, diacetone alcohol).

The amount of the solvent can be selected from the range not adversely affecting castability in the forming of a film, spinnability and handleability. Thus, based on 100 parts by weight of cellulose acetate, the solvent can be used in a proportion of, for example, about 150 to 1000 parts by weight (cellulose acetate concentration of about 10 to 40% by weight), preferably about 200 to 900 parts

by weight (cellulose acetate concentration of about 10 to 30% by weight). The concentration of the cellulose acetate in the dope is usually about 10 to 25% by weight (for example, 10 to 20% by weight).

[0044]

The dope thus obtained is useful for forming or molding of film by a casting process. In the film-formation, a cellulose diacetate or a cellulose triacetate (in particular a cellulose triacetate) is usually used. The film is prepared by casting a dope on a support, and after partial drying (semi-drying), the film is released from the support. The released film is then dried to form a film.

The support may be any of the conventional supports, for example a mirror-finished or specular metal support (e.g., a stainless steel support).

Since the cellulose acetate of the present invention has excellent releasability, the film in semi-dry state (semi-dried film) can be smoothly released from the support, with the result that a cellulose acetate film with a high degree of surface smoothness can be provided. Therefore, the method with use of the dope of the present invention is useful for improving releasability of a film from a support. Moreover, the cellulose acetate film of the present invention is outstanding in optical characteristics (yellowness, haze, and transparency).

The thickness of the cellulose acetate film can be

selected according to the intended application, for example from the range of about 5 to 500 μm , preferably about 10 to 200 μm , and more preferably about 20 to 150 μm (50 to 150 μm in particular).

The cellulose acetate of the present invention is not only useful for the production of photographic film, polarizer protective film or color filter film by the casting technique but can be used, by taking advantage of its good releasability, as a material for the production of a thin-optical film or device by, for example, the spin coating technology.

[0045]

The cellulose acetate of the present invention is superior in stability, filterability and spinnability of the dope as described above. When a fiber is produced by spinning process, a cellulose diacetate or a cellulose triacetate is usually used as a cellulose acetate. The spinning process may be carried out by a conventional method, for example, by spinning a dope from a base having many fine holes and drying the spinning yarns or threads, and if necessary, drawing or stretching the fibers. The use of the dope of the present invention in the spinning process may prevent clogging or choking of the holes or thread breakage for a long time. Therefore, the method with use of the dope of the present invention is useful for improving spinnability.

[0046]

The cellulose acetate or the dope of the present invention may contain one or more plasticizers including, for example, phosphoric acid esters such as triphenyl phosphate (TPP), tricresyl phosphate (TCP), etc.; phthalic acid esters such as dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), dioctyl phthalate (DOP), di-2-ethylhexyl phthalate (DEHP), etc.; fatty acid esters such as butyl oleate, methyl acetyl ricinolate, dibutyl sebacate, etc.; citric acid esters such as acetyl triethyl citrate (OACTE), acetyl tributyl citrate (OACTB), etc.; trimellitic acid esters, and so forth. These plasticizers can be used singly or in combination.

The cellulose acetate may further contain aging inhibitors such as an antioxidant, an ultraviolet absorber, a peroxide decomposer, a radical scavenger, a metal deactivator or sequesterant, an acid acceptor, and other additives. Where necessary, the cellulose acetate may contain such other additives as a nucleating agent, an inorganic powder (e.g., diatomaceous earth, calcium carbonate, titanium dioxide), a thermal stabilizer, a flame retardant, and a coloring agent.

[0047]

[Effects of the Invention]

By using the cellulose acetate (cellulose acetate having a free carboxyl group, cellulose acetate containing a specific acid or metal salt thereof, cellulose acetate

having a reduced content of an alkali metal salt and alkaline earth metal salt) of the present invention, it is easily releasable from the support in a casting process to provide a film with a high surface smoothness and excellent optical characteristics. Moreover, the cellulose acetate of the present invention is superior in stability, filterability and spinnability of the dope and high thermal resistance.

[0048]

[Examples]

The following examples are intended to describe this invention in further detail and should by no means be interpreted as defining the scope of the invention.

Incidentally, the releasability of the film from support in the casting process was evaluated as follows.

One-hundred (100) parts by weight of cellulose acetate was mixed with 320 parts by weight of methylene chloride, 40 parts by weight of methanol, 25 parts by weight of butanol, and 15 parts by weight of triphenyl phosphate (TPP) to prepare a dope. This dope was cast on a smooth stainless steel plate (support) in a thickness of about 1 mm at room temperature (about 20 to 25°C) and allowed to stand at room temperature for 3 to 4 minutes. Then, the releasability of the film from the support was evaluated in according to the following criteria.

○ : Smoothly released with a minimum of peel drag

and the film surface was smooth.

X : Not smoothly released but a considerable peel drag was felt, film peelings remain on the stainless steel plate.

[0049]

Comparative Example 1

One-hundred (100) parts by weight of a hardwood kraft pulp (α -cellulose content 94.5%) was sprayed with 50 parts by weight of glacial acetic acid for activation. Then, a mixture of 470 parts by weight of glacial acetic acid, 265 parts by weight of acetic anhydride, and 8.3 parts by weight of sulfuric acid was added to the activated mixture, and the esterification reaction was carried out in the conventional manner. Thereafter, the hydrolysis reaction was carried out, and thermal stabilizers (calcium acetate and magnesium acetate) were added to the resultant hydrolyzate to provide a cellulose triacetate (CTA, a degree of acetylation of 61.3% and a viscosity average degree of polymerization of 301 (calcium content of 98 ppm (4.9×10^{-6} ion equivalent), magnesium content of 16 ppm (1.3×10^{-6} ion equivalent))). This CTA had a YI of 7.1, a haze value of 2.6, and a transparency of 78%.

The resulting CTA was used to prepare a dope. When the releasability of the film in the spinning process was evaluated, the rating was "x".

[0050]

Examples 1 and 2, and Comparative Example 2

To citric acid solutions having different concentration each other, 50g of the resulting CTA flakes obtained in Comparative Example 1 were added. The each mixture was stirred for 1 hour at room temperature (20 to 25°C) and dipped for treatment of the CTA with citric acid. The CTA flakes were filtrated off, washed with water and vacuum dried to produce CTA flakes containing the following content of citric acid per 1 gram.

[0051]

Example 1: the citric acid content of 7.7×10^{-7} mole, YI 7.0, haze value 2.2, transparency 85%

Example 2: the citric acid content of 6.8×10^{-8} mole, YI 7.0, haze value 2.4, transparency 81%

Comparative Example 2: the citric acid content of 5.5×10^{-9} mole, YI 7.1, haze value 2.6, transparency 75%

The resulting CTA flake treated with citric acid was used to prepare a dope in the same manner as in Comparative Example 1. When the releasability of the film in the casting process was evaluated, the rating of Examples 1 and 2 was "○", and the rating of Comparative Example 2 was "x".

[0052]

Example 3

To 97g of the dope prepared by Comparative Example 1 (the content of CTA 19.4g), 11.8mg of citric acid was added and mixed to produce a dope containing citric acid. Using this dope, when the releasability of the film in the

casting process was evaluated as the same manner as in Comparative Example 1, the rating was "○".

[0053]

Example 4

Using the CTA flake obtained in Comparative Example 1, a dope was prepared as in Comparative Example 1. To 97g of the dope (the content of CTA 19.4g), 35.3mg of calcium citrate·4H₂O was added and mixed to produce a dope containing the citric acid salt. Using this dope, when the releasability of the film in the casting process was evaluated as the same manner as in Comparative Example 1, and the rating was "○".

[0054]

Comparative Example 3

One-hundred (100) parts by weight of a hardwood kraft pulp (α -cellulose content 94.5%) was sprayed with 50 parts by weight of glacial acetic acid for activation. Then, a mixture of 445 parts by weight of glacial acetic acid, 265 parts by weight of acetic anhydride, and 8.3 parts by weight of sulfuric acid was added to the activated mixture, and the esterification reaction was carried out in the conventional manner. Thereafter, the hydrolysis reaction was carried out to provide, without adding a thermal stabilizer (calcium acetate and magnesium acetate), a cellulose triacetate with a degree of acetylation of 60.8% and a viscosity average degree of polymerization of 313 (CTA, calcium content of 0 ppm, magnesium content of 7.3

ppm (0.61×10^{-6} ion equivalent), the sodium content of 0 ppm per 1 gram of CTA). This CTA had a YI of 3.5, a haze value of 2.7, and a transparency of 78.2%.

[0055]

Examples 5 to 7, and Comparative Examples 4 and 5

To calcium hydroxide solution, magnesium hydroxide solution or sodium acetate solutions which have different concentration each other, the flake of Comparative Example 3 was dipped for treatment. The each CTA flake was filtrated off and dried to produce CTA flake containing the following content of metal components per 1 gram. Incidentally, Ca, Mg and Na represent calcium, magnesium and sodium, respectively. The content of these metals per 1 gram CTA in the term of ion equivalent ($\times 10^{-6}$ equivalent unit) shows in parentheses.

[0056]

Example 5: Ca content 10 ppm (0.5), Mg content 5.6 ppm (0.47), Na content 0 ppm

Example 6: Ca content 6.5 ppm (0.33), Mg content 22 ppm (1.8), Na content 0 ppm.

Example 7: Ca content 2 ppm (0.1), Mg content 4.3 ppm (0.36), Na content 53 ppm (2.3)

Comparative Example 4: Ca content 98 ppm (4.9), Mg content 16 ppm (1.3), Na content 0 ppm

Comparative Example 5: Ca content 129 ppm (6.5), Mg content 93 ppm (7.8), Na content 0 ppm

Using CTA treated with dipping as mentioned above,

a dope was prepared and the releasability of the film was evaluated as in Comparative Example 1. As a result, the rating of Examples 5 to 7 were "○" and the rating of Comparative Examples 4 and 5 were "x".

When the slurry pH of Comparative Example 3, Examples 5 to 7 and Comparative Example 5 were determined, the resulting values were as follows.

Comparative Example 3: 4.26

Example 5: 4.51

Example 6: 4.83

Example 7: 5.03

Comparative Example 5: 6.45

When the releasability of cellulose acetates of Comparative Example 3, Examples 5 to 7 and Comparative Example 5 were evaluated, the ratings of Comparative Example 3 and Examples 5 to 7 were "○", and the rating of Comparative Example 5 was "x".

The heat resistance of cellulose acetates of Comparative Example 3, Examples 5 to 7 and Comparative Example 5 were evaluated in according to the following criteria.

○ : when heated at 60°C for drying, deterioration and discoloration are not observed

x : when heated at 60°C for drying, there was deterioration and discoloration

Comparative Example 3 and Examples 5 to 7 showed the heat resistance level "○" and Comparative Example 5 showed

the heat resistance level "x"

[0057]

Example 8

One-hundred (100) parts by weight of a softwood sulfite pulp (α -cellulose content 94.5%) was sprayed with 50 parts by weight of glacial acetic acid for activation. Then, a mixture of 445 parts by weight of glacial acetic acid, 265 parts by weight of acetic anhydride, and 8.3 parts by weight of sulfuric acid was added to the activated mixture, and the esterification reaction was carried out in the conventional manner. Thereafter, the hydrolysis reaction was carried out and calcium acetate and magnesium acetate were added to the resulting hydrolysis to provide a cellulose triacetate with a average degree of acetylation of 61.3% and a viscosity average degree of polymerization of 310 (CTA, Ca content of 10 ppm (0.5×10^{-6} ion equivalent), Mg content of 5.3 ppm (0.44×10^{-6} ion equivalent) per 1 gram of CTA). This CTA had a YI of 6.6, a haze value of 2.0, and a transparency of 83%.

The releasability was evaluated as in Comparative Example 1, and the rating was "○".

[0058]

Example 9 and Comparative Example 6

Except that a softwood sulfite pulp (α -cellulose content 96.1%) was used instead of the starting pulp used in Example 8, the esterification reaction was carried out in the same manner as Example 8. Thereafter, the

hydrolysis reaction was carried out, and calcium acetate and magnesium acetate were added to the resultant mixture to provide a cellulose triacetate with a average degree of acetylation of 55.2% and a viscosity average degree of polymerization of 299 (CDA, the metal component content was represented as follows). The content of these metals per 1g CDA in the term of ion equivalent ($\times 10^{-6}$ equivalent) represents in parentheses.

Example 9: the Ca content of 10 ppm (0.44), the Mg content of 6.2 ppm (0.52); a haze value of 1.9, transparency of 82.5%.

Comparative Example 6: the Ca content of 125 ppm (6.3), the Mg content of 18 ppm (1.5); a haze value of 6.3, transparency of 73%.

The CDA obtained by Example 9 and Comparative Example 6 was used to prepare 30% by weight of acetone solution (dope). When the spinnability of the dope was evaluated in according to the following criteria as the stability of the dope in the course of time, the ratings of CDA in Example 9 was "○", and the rating of CDA in Comparative Example 6 was "x".

○ : the dope was stable for a long time, and when filtering, there was no choking of the holes.

x : the dope became white turbid, thus the stability of the dope lowered, and when filtering, there was choking of the holes.

[Document Name] ABSTRACT

[Abstract]

[Object(s)] To provide a cellulose acetate having high film-releasability from a support and excellent optical characteristics.

[Means to Solve the Problems] Using the dope containing the following cellulose acetate (1), (2), or (3), a film is prepared by the casting process:

(1) a cellulose acetate having carboxyl groups binding to a cellulose acetate and/or a hemicellulose acetate, wherein said carboxyl groups are in an acidic form;

(2) a cellulose acetate containing at least one member selected from the group consisting of an acid having an acid dissociation exponent pK_a of 1.95 to 4.50 in water [e.g. citric acid], or a salt thereof (an alkali metal salt of said acid and an alkaline earth metal salt of said acid);
or

(3) a cellulose acetate containing an alkali metal or an alkaline earth metal wherein the total content of an alkaline metal and an alkaline earth metal in 1 gram of the cellulose acetate is from an effective amount to 5.5×10^{-6} equivalent (in terms of ion equivalent). The above cellulose acetate is also useful for spinning process. The cellulose acetate includes a cellulose diacetate and a cellulose triacetate.

[Selected Fig.] none

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